through a small 1-in. Florisil column to remove any organic tars, colloidal silver, or platinum. A clear, pale yellow solution was eluted with dichloromethane and subsequent addition of diethyl ether yielded pale yellow needles of $[PtCH_3\{P(CH_3)_2(C_6H_5)\}_2(NH{=}C(O\text{-}n\text{-}C_3H_7)C_6F_4C{\equiv}N)PtCH_3\{P(CH_3)_2(C_6H_5)\}_2][BF_4]_2$ (0.190 g).

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Polarized Crystal Spectra of Tris(diethyldithiophosphato)vanadium(III), -chromium(III), and -cobalt(III)[1a]

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The electronic structures of tris(diethyldithiophosphato)vanadium(III), -chromium(III), and -cobalt(III) have been investigated using the polarized ligand field spectra of the chromophores doped into the lattice of the colorless crystal of tris(diethyldithiophosphato)indium(III). Spectra were measured at 300, 80, and 5°K. Molecular polarizations (perpendicular and parallel to the C_3 axes) have been calculated from the crystal spectra observed with light polarized along extinction directions in the monoclinic crystal. The selection rules allow an independent check of these calculations which confirms the validity of the method. Polarizations indicate close adherence to trigonal (D_3) selection rules (with the exception of $V(dtp)_3$ at low temperatures) despite the C_1 site symmetry of the metal ions. Trigonal splittings, as indicated by band maxima in the lower energy manifold of each spectrum, are 0.6 kK for $Cr(dtp)_3$ and $Co(dtp)_3$ and considerably less than this for $V(dtp)_3$, with the E component at higher energy in each case. The $Cr(dtp)_3$ spectrum has been fitted to a crystal field model which indicates by its unusually large ratio of C/B the predominance of the σ-delocalization mechanism in this complex.

Introduction

Metal complexes of diethyldithiophosphate (dtp^-) have been of considerable practical and theoretical interest during the past decade. Their applications, as diverse as carcinostatic agents[2] and corrosion-inhibiting oil additives[3] have been explored. Studies of their spectral,[2,4-16] magnetic,[17-21] and structural properties[3,11,22-26] have engaged the interest of numerous investigators in both academic and industrial laboratories. In this paper we describe the results of our polarized single-crystal spectra of three complexes of the formula $M(dtp)_3$, M = V(III), Cr(III), and Co(III), doped into the colorless host lattice $In(dtp)_3$. The general trigonal symmetry predicted for these bidentate ligand complexes has been confirmed in the structure of the host.[22] Although some additional distortion of the coordination sphere is evident in this lattice, as well as in the isomorphous structure of $V(dtp)_3$,[11] the trigonal distortion is predominant and provides the framework for the analysis of the spectral results.

The solution spectra of the chromium and cobalt compounds and of other dtp^- complexes were first reported by Schäffer[8] and by Jørgensen,[4,6] who commented on the pronounced dichroism exhibited by the $Cr(dtp)_3$ crystals and speculated on the source of the unusually high molar absorptivities of both the $Cr(dtp)_3$ and $Co(dtp)_3$. A preliminary report of the $V(dtp)_3$ crystal and solution spectra has recently appeared,[11] though the temperature dependence, detailed polarization results, and trigonal splitting parameters have not been previously reported.

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Experimental Section

Synthesis.—The compounds In(dtp)$_3$ and Co(dtp)$_3$ were prepared as described by Jørgensen.[4,6] The preparation of Cr(dtp)$_3$ is also given in the literature.[27] V(dtp)$_3$ is both oxygen and water vapor sensitive and was prepared on a vacuum line by the following procedure. The free acid Hdtp was vacuum distilled into a reaction flask containing a carefully degassed solution of VCl$_3$ in Spectrograde methanol. The solvent was drawn off slowly under vacuum. Bright red pseudohexagonal plates similar to those described by Furlani, *et al.*,[11] were obtained after a few days. Very careful glove bag techniques can also be used for this synthesis. The complex was recrystallized from methanol in the absence of oxygen. In(dtp)$_3$, Cr(dtp)$_3$, and Co(dtp)$_3$ crystals were grown from either methanol, 95% ethanol, or acetone solutions and doped In(dtp)$_3$ crystals were grown from methanol solution.

Diethyldithiophosphoric acid, technical grade, was obtained from Aldrich Chemical Co. Purification of the ligand was accomplished in the process of multiple recrystallizations of the complexes. Cobalt chloride, CoCl$_2$·6H$_2$O, and chromium chloride, CrCl$_3$·6H$_2$O, reagent grade, were obtained from J. T. Baker Chemical Co. Indium metal was obtained from Research Organic/Inorganic Chemical Corp.

Measurement and Treatment of Spectral Data.—The equipment and techniques used in the measurement and treatment of the crystal spectral data have been for the most part described previously.[28] Because of the high molar absorptivities of the dtp$^-$ complexes the spectra reported were all measured in doped In(dtp)$_3$ crystals. Since the concentration of the chromophores in the doped crystals was not known exactly, the crystal molar absorptivities were estimated from the assumption that the solution values are composed of $^1/_3\epsilon_\pi + {}^2/_3\epsilon_\sigma$, where ϵ_π and ϵ_σ are the intrinsic molar absorptivities for light polarized parallel and perpendicular to the molecular C_3 axis. Spectra were also measured in rigid-glass films made by dissolving the complexes in a chloroform solution of poly(methyl methacrylate) and allowing the solvent to evaporate.

Calculation of Molecular Spectra.—In(dtp)$_3$ crystallizes as thin, colorless, pseudohexagonal plates in the space group *Cc*.[22] The (001) crystal face is prominent. The unit cell parameters are a = 8.61 Å, b = 18.81 Å, c = 17.85 Å, β = 92.2°, d_{calcd} = 1.54 g/cm^3, and Z = 4. As shown in the crystal structure determination, although the metal ion is close to being at a site of twofold symmetry (in which case the space group would be $C2/c^{11}$), the excessively large thermal ellipsoids of key atoms resulting when refinement in $C2/c$ is attempted indicate that the complex does not in fact have the C_2 site symmetry at first apparent. Refinement in space group *Cc*, on the other hand, produces a much more consistent set of thermal parameters.[22] The site symmetry of the metal is then C_1. Nevertheless, the molecule has approximately D_3 symmetry with the indium–sulfur distances varying randomly between 1.87 and 2.14 Å. Distortion toward trigonal-prismatic symmetry is minimal. The intraligand SInS angle, which is some measure of the trigonal distortion, averages 78° and the average polar angle of the S–In bonds is 56° 11′ as compared to 90° and 54.7°, respectively, in a regular octahedral complex. Lack of conjugation in the chelate ring is indicated by the two different P–S bond distances; these average 1.91 and 2.08 Å for the three ligands. The molecular structure of the pure V(dtp)$_3$[11] crystal appears to support the assumption that the transition metal analogs of In(dtp)$_3$ are essentially isostructural with it. The bond distances and angles in V(dtp)$_3$, which appears essentially isomorphous to In(dtp)$_3$, differ as expected for the smaller V^{3+} ion. (V–S = 2.435–2.473 Å; S–V–S = 82°).[11]

Spectra were measured with light incident on the natural (001) face. The light was polarized along the extinction directions which, as required by symmetry, are parallel to the a and b axes in this orientation. Although the two sets of molecular C_3 axes are misaligned by 4.4°, they are symmetrically disposed with respect to the a and b axes. Both C_3 axis orientations make angles of 39.5° with the a axis and 87.8° with the b axis. This leads to the relationships

$$a_b = a_\pi \cos^2 87.8° + a_\sigma \sin^2 87.8°$$

$$a_a = a_\pi \cos^2 39.5° + a_\sigma \sin^2 39.5°$$

therefore

$$a_b = 0.0015a_\pi + 0.999a_\sigma$$

$$a_a = 0.595a_\pi + 0.405a_\sigma$$

The reciprocal matrix of the coefficients is

$$\begin{pmatrix} -0.683 & 1.683 \\ 1.002 & -0.002 \end{pmatrix}$$

therefore

$$a_\pi = -0.683a_b + 1.683a_a$$

$$a_\sigma = 1.002a_b + 0.002a_a \simeq a_b$$

In these equations a_a and a_b are the absorbances measured with the electric vector parallel to the a and b crystal axes, whereas a_π and a_σ are the corresponding values which would (assuming an oriented gas model) be observed if the electric vector were parallel (π) and perpendicular (σ) to the molecular C_3 axes.

The results can be summarized with respect to the observed crystal spectra by noting that the b spectrum is an essentially pure σ spectrum and that the a spectrum is 40% σ + 60% π. In the case of bands predicted to be completely polarized, this latter observation is useful in judging the degree of adherence to selection rules prior to calculation of the molecular spectra. These equations are entirely analogous to those of Piper.[29] Similar calculations of molecular spectra from low-symmetry crystal measurements have recently been reported.[28]

Results

The polarized visible spectra, measured at 300 and 80°K, of In(dtp)$_3$ crystals doped with V(dtp)$_3$, Cr(dtp)$_3$, and Co(dtp)$_3$ are shown in Figures 1 and 2.

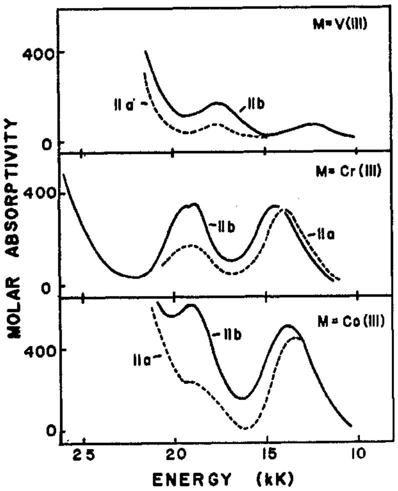

Figure 1.—Crystal spectra of M(dtp)$_3$ at 300°K.

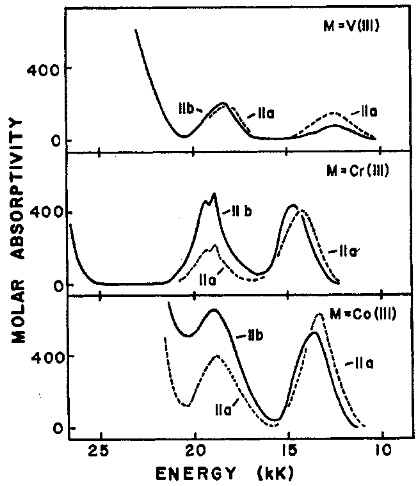

Figure 2.—Crystal spectra of M(dtp)$_3$ at 80°K.

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[27] D. E. Goldberg, W. C. Fernelius, and M. Shamma, *Inorg. Syn.*, **6**, 142 (1960).

[28] P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, **10**, 1046 (1971).

[29] T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).

Molecular spectra calculated as described above are illustrated in Figures 3 and 4. The intensity ratios of the two crystal polarizations of the second spin-allowed bands in the three spectra at 300, 80, and 5°K are shown in Table I. Note that the ratios remain reasonably constant with temperature for Cr(dtp)$_3$ and Co(dtp)$_3$ but change drastically for V(dtp)$_3$. The band assignments, energies, and estimated integrated band intensities are shown in Table II. The intensities are estimated on the assumption that the solution and crystal dipole strength are the same at ambient temperature. From this, the approximate molar absorptivities and intensities of the bands in the 300° crystal spectra can be calculated. Using the same crystal then, the intensities at lower temperatures are obtained. The data at 300 and 80°K represent averages of five determinations whereas the 5°K results are those of single runs. The most striking feature of this table is the increase in I for the π-allowed bands as the temperature is lowered. Table III summarizes the crystal field parameters for the M(dtp)$_3$ complexes in comparison with similar complexes.[30,31] Of particular interest are the values of v the trigonal splitting parameter. The polarized ultraviolet spectrum at 80°K of V(dtp)$_3$ is shown in Figure 5 illustrating the relatively low-intensity charge-transfer bands in this complex.

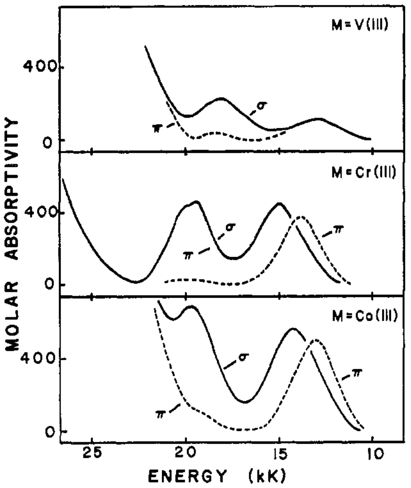

Figure 3.—Molecular spectra of M(dtp)$_3$ at 300°K.

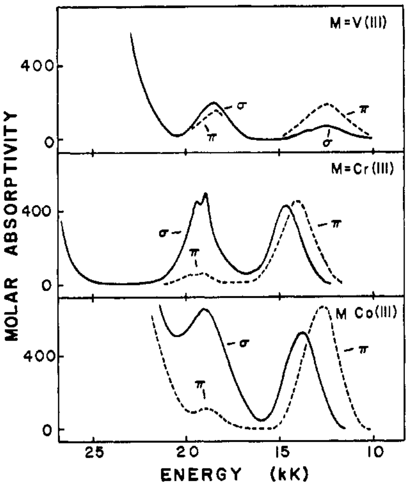

Figure 4.—Molecular spectra of M(dtp)$_3$ at 80°K.

Table I

Polarization Ratio I_a/I_b for Second-Spin-Allowed Bands in M(dtp)$_3$ Crystal Spectra

	I_a/I_b		
M	300°K	80°K	5°K
V(III)	0.49	0.91	1.10
Cr(III)	0.41	0.47	0.58
Co(III)	0.34	0.49	0.43

Table II

Band Assignments and Integrated Band Intensities in M(dtp)$_3$ Crystal Spectra

Excited state			300°K		80°K		5°K	
O_h	D_3		ν_{max}[a]	I[b]	ν_{max}[a]	I[b]	ν_{max}[a]	I[b]
			M = V(III)					
$^3T_{2g}$	^3E		12.75	11	12.75	6.5	12.75	7.1
	$^3A_1$		12.65	10	12.71	27	12.75	21
	?		14.6		14.2		14.2	
$^3T_{1g}$	^3E		18.10	19	18.35	15	18.44	14
	$^3A(C_3)$		17.90	(5)	17.90	20	17.93	33
CT		$(\parallel a)$	23.09	196	23.53	123		
		$(\parallel b)$	22.99	243	23.39	195		
CT	($^3A_2$?)	$(\parallel a)$	26.30	82	26.23	128		
		$(\parallel b)$	26.45	154	26.08	128		
CT		$(\parallel a)$			(28.9)	45		
		$(\parallel b)$			29.3	123		
			M = Cr(III)					
^2E_g	^2E		13.0	<1	13.1	<1	13.2	<1
$^2T_{1g}$	^2E, $^2A_2$		13.5	<1	13.6	<1	13.7	<1
$^4T_{2g}$	$^4A_1$		13.86	53	14.03	84	14.37	54
	^4E		14.50	65	14.70	42	14.61	55
	?		~17		~17		~17	
$^4T_{1g}$	^4E		18.68	57[c]	18.75	53[c]	18.79	40[c]
$^2T_{2g}$	^2E		19.25		19.25		19.20	
			M = Co(III)					
$^1T_{1g}$	$^1A_2$		13.08	89	13.19	129	13.19	129
	^1E		13.60	86	13.78	66	13.79	55
$^1T_{2g}$	^1E		(18.5)	(102)	18.75	(103)	18.75	93

[a] Energy, ν, in kK. [b] Integrated band intensity, $I = (1/\nu_{max})\cdot\int\epsilon d\nu$, in units of molar absorptivity. [c] Includes intensity shared with ^2E band.

Table III

Ligand Field Parameters for M(dtp)$_3$ and Other Trigonal Complexes

M	Parameter[a]	M(dtp)$_3$[b]	M(ox)$_3^{3-}$ [30]	M(acac)$_3$[31]
V(III)	Dq	1.36	1.75	1.80
	B	0.427		
	v [= +2(E−A$_1$)]	+0.08	+0.690	+2.70
Cr(III)	Dq	1.45	1.77	1.81
	B	0.389		
	C	3.26		
	v [= −2(E−A$_1$)]	−1.34	−0.810	−1.50
Co(III)	Dq	1.42	2.00	2.10
	B	0.378		
	v [= −2(E−A$_2$)]	−1.18	+0.300	−1.80

[a] In kK. [b] At 80°K.

Discussion

Effective Electronic Symmetry.—Jørgensen[4,6,13] and others[12] have assigned the transitions of the V(dtp)$_3$, Cr(dtp)$_3$, and Co(dtp)$_3$ spectra based on solution data in terms of the parent octahedral symmetry group. These assignments are verified by the polarized data presented here. Since, as shown in the crystal structure of the In(dtp)$_3$ host lattice,[22] the predominant distortion of the coordination sphere around the metal ion

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(30) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).

(31) T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

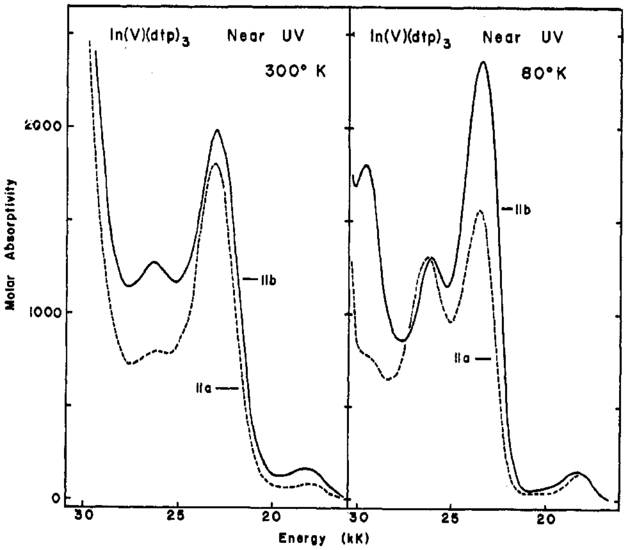

Figure 5.—Near-ultraviolet crystal spectra of In(V)(dtp)$_3$.

is the compression of the intraligand S–M–S angle, it is reasonable to attempt analysis of the spectra of transition metals doped in the lattice in terms of D_3 symmetry. (Although if the same intraligand S–S distance is assumed, the smaller transition metals might be predicted to form somewhat larger intraligand S–M–S angles,[11] trigonal symmetry is still the most obvious framework within which to work.) Three aspects of such an analysis are of particular interest: one, the degree of adherence to trigonal selection rules; two, the perturbation of the trigonal symmetry by smaller distortions and lattice site symmetry effects; and three, the magnitude of the apparent trigonal splitting.

To test the hypothesis of trigonal symmetry the spectra were subjected to analysis making the usual assumptions that the guest molecules substitute into the lattice isomorphously for those of the host and that the chromophores do not interact with each other. The details of the geometrical relationships are given above. As it happens, the *second* predicted spin-allowed octahedral d–d band in each of the ions included here should be completely polarized when the symmetry is lowered to D_3; *viz.*

	O_h	D_3
V(III); d^2	$^3T_{1g} \leftarrow {}^3A_{2g}$	$^3A_2 \not\leftarrow, {}^3E \xleftarrow{\sigma} {}^3A_2$
Cr(III); d^3	$^4T_{1g} \leftarrow {}^4A_{2g}$	$^4A_2 \not\leftarrow, {}^4E \xleftarrow{\sigma} {}^4A_2$
Co(III); d^6	$^1T_{2g} \leftarrow {}^1A_{1g}$	$^1A_1 \not\leftarrow, {}^1E \xleftarrow{\sigma} {}^1A_1$

That is to say, for each spectrum, in the upper-band manifold the observed intensity in the *a*-polarized spectrum will be 40% of that in the *b*-polarized spectrum since all intensity in that band should result from interaction of light with the molecules in such a way that the electric vector $\vec{E}$ is perpendicular to the C_3 axes (σ). This affords a quick comparison between the three ions, as well as a test of the proposed selection rules. The results are summarized in Table I. The ratios generally give strong support to the D_3 effective electronic symmetry assumption. The low value for the cobalt(III) compound at room temperature is not reliable because of the lack of resolution of the band from the charge-transfer absorption.

The calculated molecular spectra at ambient temperature in Figure 3 further illustrate the strength of the selection rules which govern the intensities. The one notable exception to the adherence to the D_3 selection rules is found in the increase of the π intensity of the upper band in V(dtp)$_3$ at 80° and lower (see below). Some slight, but perhaps significant, trend in the same direction is noted in the ratios for the chromium and cobalt complexes (Table I). No significant change in any of the spectra was noted below 80°—either in energies or in intensities.

The above observations coupled with the relatively small temperature dependence of the intensities of the bands (Table II) seem to prove conclusively that the source of the large intensities in these formally d–d transitions is the static distortion of the ligand field and not vibronic effects to any appreciable extent.

Trigonal Splittings.—Having used the upper-band systems in the spectra to verify the effective symmetry of the chromophores, we may now use the lower bands to determine the trigonal splitting. This should work for each of the complexes since the lower energy band in each case should have an allowed σ and π component; *viz.*

	O_h	D_3
V(III); d^2	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^3A_1 \xleftarrow{\pi}, {}^3E \xleftarrow{\sigma} {}^3A_2$
Cr(III); d^3	$^4T_{2g} \leftarrow {}^4A_{2g}$	$^4A_1 \xleftarrow{\pi}, {}^4E \xleftarrow{\sigma} {}^4A_2$
Co(III); d^4	$^1T_{1g} \leftarrow {}^1A_{1g}$	$^1A_2 \xleftarrow{\pi}, {}^1E \xleftarrow{\sigma} {}^1A_1$

The difference in energy $E(\mathrm{E} \leftarrow \mathrm{A}) - E(\mathrm{A} \leftarrow \mathrm{A})$ is defined[32] as $+v/2$ for vanadium(III) and $-v/2$ for chromium(III) and cobalt(III). The other frequently used trigonal field parameter K is $-v/3$. Observation of intensity in the π polarization of the upper band manifold would allow evaluation of the second-order trigonal parameter $v' = K'$[32] but this is not meaningful in the chromium and cobalt spectra because of the virtually complete polarization and in the vanadium complex because of the ambiguity of the polarization (*vide infra*).

The trigonal splitting parameters v evaluated from the derived *molecular* spectra are given in Table III along with previously reported trigonal splitting data for the corresponding M(ox)$_3^{3-}$ and M(acac)$_3$ complexes for comparison. The M(dtp)$_3$ data reflect the fact that in each of the three spectra the E level is above the A. Trigonal splitting parameters for vanadium(III), chromium(III), and cobalt(III) in sulfur donor complexes have not been reported before. Since the sign and magnitude of v (and K) depend on the radial parameters as well as the distortion of the coordination sphere, comparison of trigonal parameters beyond rather strict limits does not seem useful. For example, the comparison between the M(dtp)$_3$ data and those for the M(ox)$_3^{3-}$ ions, which also involve compression of the intrachelate angles, is not very close. Although solution spectra of the dithiooxalates have been measured,[33] the crystal spectra have not been reported.

Evaluation of Other Crystal Field Parameters and Assignment of Spin-Forbidden Bands.—The values for Dq and B (and, for Cr(dtp)$_3$, C) given in Table III generally agree with those evaluated from solution data, the shift of Dq to slightly higher values being the normal effect of lower temperature. However, the low-temperature glass and crystal spectra do shed additional

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[32] D. S. McClure, *Solid State Phys.*, **9**, 484 (1959).

[33] R. L. Carlin and F. Canziani, *J. Chem. Phys.*, **40**, 371 (1964).

light on some of the spectral assignments which should be noted.

V(dtp)$_3$.—The analysis and assignments presented here presume that the ground state of V(dtp)$_3$ is $^3A_2$. Although this has not yet been verified by magnetic measurements, the polarization data at ambient temperature strongly support this conclusion. It should be mentioned in passing that the earlier brief analysis of the V(dtp)$_3$ crystal spectrum by Furlani, *et al.*,[11] in terms of C_3 symmetry does not appear compatible with our results, since in C_3 symmetry the virtually complete polarization of the higher energy band observed at ambient temperature is not predicted. However, the assumption of D_3 selection rules and an A_2 ground state, as mentioned above, does give the correct prediction. An E ground state in either C_3 or D_3 symmetry would not lead to the observed (ambient temperature) polarization.

The strong polarization of the $^3T_{2g}$ manifold in the V(dtp)$_3$ spectrum disappears when the crystal is cooled to 80° and lower. Possible causes of such a change in polarization include lowering of the effective symmetry to C_3 or C_2, a change in electronic ground state with the symmetry remaining D_3, or a significant change in thermal population of levels within the $^3T_{1g}(O_h)$ ground-state manifold. Considering first the possible effects of thermal population changes, it is noted that the depopulation of a higher E state would *remove* π intensity in the $^3T_{2g}$ manifold since an $E \leftarrow E$ transition is both π and σ allowed. On the other hand, depopulation of a higher A_2 state would *enhance* π intensity in this band, which is what is observed. However, such an analysis would predict considerable π intensity even at 300° and this is *not* observed. So thermal population effects with *either* A_2 or E as ground state do not seem to explain the data adequately. If instead of merely depopulating the upper level of the $T_{1g}(O_h)$ manifold, we consider the possibility that *the ground state changes* from A_2 to E or that v approaches zero, as the temperature is lowered, the dramatic change in polarization can be rationalized. The detailed temperature dependence of magnetic susceptibility should shed light on this question. However, the data in Table II do indicate that for V(dtp)$_3$ the trigonal splitting is small ($v > 0$; $E > A$) and decreases at lower temperatures.

Finally, we should also consider the possibility of effective symmetry lowering as the temperature is decreased. Electric dipole selection rules for either C_3 or C_2 predict σ and π intensity in both spin-allowed band manifolds. There does not seem to be a way to interpret the spectral data so as to favor either possibility over the other.[34] Such a lowering of symmetry might be induced by the site symmetry effects (C_1). This is particularly applicable in this case because of the striking difference in the ionic radius of V^{3+} as compared to the other trivalent ions of the first transition series (see Table IV). The larger V^{3+} ion might be supposed to "feel" the stress of the thermal contraction of the lattice to a much greater extent than the smaller Cr^{3+} and Co^{3+} ions. Choosing between this possibility and the change of the ground states in D_3 symmetry is not possible with the data available at this time.

Table IV

Crystal Radii of Trivalent Ions

M^{3+}	Radius,[a] Å
V^{3+}	0.74
Cr^{3+}	0.63
Co^{3+}	0.63

[a] "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1965.

At low temperature, the spectrum of V(dtp)$_3$ reveals none of the detail that might be expected for this d^2 complex. The intraconfigurational triplet–singlet transitions associated with the $^1T_{2g}$, ^1E_g, and $^1A_{1g}$ octahedral levels are not observed even at 5°K in either crystals or rigid glasses. These spin-forbidden transitions should give rise to narrow, sharp, weak bands as have been observed in other spectra of vanadium(III) complexes at low temperatures.[35] Assuming the usual relationship $C = 4B$[36] would predict their positions at about 6.4, 6.4, and 10.9 kK, respectively.[37] However, inferences drawn from the Cr(dtp)$_3$ spectrum (*vide infra*) suggest that in fact $C \cong 8B$ may be more realistic in these complexes. If this is so, then the intraconfiguration bands would be found at 9.0, 9.0, and 14.4 kK. In any case, no bands attributable to these transitions were observed.

Of other expected ligand field transitions in the spectrum of V(dtp)$_3$ the only other one likely to be seen is that associated with the $^3A_2(^3A_{2g})$ level. This transition is forbidden as a two-electron process in the strong-field limit and (at least at ambient temperature) would seem to be symmetry forbidden as well. Its calculated position at 26 kK has led to its association with the intense maximum at 26.28 kK.[11] We have carefully examined this area of the V(dtp)$_3$ spectrum using doped In(dtp)$_3$ crystals and found, at 80°K, not one, but two such medium-intensity maxima at 26.0 and 29.0 kK (Figure 5). Either of these might be the $^3A_2$ band but one must be a charge-transfer transition. In light of the forbidden nature of the $^3A_2 \leftarrow {}^3A_2$ transition, it seems most likely that both are charge transfer. Interestingly enough, however, the temperature dependence of the polarization of the 26-kK band *is* similar to that of the $^3T_{1g}$ manifold, *i.e.*, allowed only in the σ polarization at ambient temperature but unpolarized at 80°K and below.

Observation previously reported of extensive vibronic structure in the V(dtp)$_3$ spectrum[11] could not be confirmed despite diligent effort, at either 300, 80, or 5°K, in any part of the spectrum in crystals, glasses, or solution. This is consistent with results for the other trigonal dtp$^-$ complexes, although the centrosymmetric Ni(dtp)$_2$ exhibits extensive vibronic structure.[15]

Finally, one additional feature of the V(dtp)$_3$ spectrum is of interest. A broad low-intensity band is partially resolved on the high-energy side of the $^3T_{2g}$ manifold at *ca.* 14 kK. This shoulder does not seem to be very temperature dependent. Walker and Carlin[38] ascribed a very similar feature in the $V(H_2O)_6^{3+}$ spectrum to rhombic distortion. However, in V(dtp)$_3$, evidence points to D_3 symmetry at ambient temperature and the lack of temperature dependence of the energy of the

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[34] After completion of this work Furlani and coworkers published a more complete account of their work on the spectrum of V(dtp)$_3$ acknowledging the possibility of interpretation in D_3 symmetry: C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970).

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[38] I. M. Walker and R. L. Carlin, *ibid.*, **46**, 3931 (1967).

shoulder would seem to indicate that its presence is not connected with the phenomenon that causes the change in polarization of the $^{3}T_{1g}$ manifold. Coincidentally, the transition to the $^{1}A_{1}$ level should occur at 14.4 kK (*vide supra*), but this broad shoulder cannot be assigned reasonably to such an intraconfigurational transition. The possibility that the shoulder is caused by a minute impurity of $Co(dtp)_3$ is not impossible, but no other evidence for cobalt contamination could be found. This leaves us with no very attractive explanation for this shoulder.

Cr(dpt)$_3$.—Of special interest in chromium(III) compounds are the several quartet–doublet transitions usually observed in both absorption and emission. In ruby[39,40] and in $NaMgCr(ox)_3 \cdot 9H_2O$,[30] for example, transitions involving the $^{2}E_{g}(^{2}G)$ and $^{2}T_{1g}(^{2}G)$ octahedral states are assigned to distinct and very narrow absorption and emission bands. Efforts to locate these lowest energy predicted transitions in $Cr(dtp)_3$ have apparently not been successful. Although there has appeared a report of observation of emission at 11 kK,[41] recent attempts to verify this have been fruitless.[42] Efforts to detect other emission have also failed.[42] Virtually the only choice for assignment of these two closely spaced quartet–doublet transitions is the two rather broad shoulders on the low-energy side of the $^{4}T_{2g} \leftarrow {}^{4}A_{2g}$ manifold, at 13.1 and 13.6 kK. Jørgensen has also suggested this assignment.[4] Support for this choice is obtained by evaluating Dq and B from the d^3 Tanabe–Sugano diagram. The B obtained, 0.389, is also consistent with those found for other dtp^- complexes (Table III). Furthermore, two other spin-forbidden transitions are predicted in the observable region by this very approximate initial fitting: $^{2}T_{2g}(^{2}H) \leftarrow {}^{4}A_{2g}$ and $^{2}A_{1g}(G) \leftarrow {}^{4}A_{2g}$. It appears that the absorption associated with $^{2}T_{2g}$ should occur in the vicinity of the $^{4}T_{1g}$ manifold, while that of the $^{2}A_{1g}$ transition should be 5–6 kK to higher energy. No other transitions than those mentioned above are predicted below the observed onset of charge transfer.

The features in the $Cr(dtp)_3$ spectrum to be considered in completing the assignment are the split peak of the second major band (18.70 and 19.25 kK) and a vague shoulder at 17 kK. Considering the split in the band maximum there are conceivably six reasonable explanations: (1) quartet–doublet mixing between $^{4}T_{1g}$ and $^{2}T_{2g}$ or $^{2}A_{1g}$, (2) trigonal splitting, (3) Jahn–Teller excited-state splitting (dynamic), (4) rhombic splitting (C_2) (static), (5) spin–orbit splitting, and (6) emission at a lower frequency pumped efficiently only at the center of the 19-kK band. All but the first of these can be ruled out on the basis of the data available.

If trigonal splitting were responsible, only one of the components would be allowed ($^{4}E \leftarrow {}^{4}A_{2}$), whereas both are observed as σ polarized within experimental error. Additional distortion to C_2 symmetry in the excited state—either static or dynamic—would predict depolarization of the band (in contrast to experiment). Spin–orbit splitting of such magnitudes is unheard of in chromium(III) compounds and is even less likely in this case if there is a reduction in λ comparable to that in B.

The remote possibility that the effect observed at 19 kK is really an emission "hole" in the band was experimentally ruled out by measuring the spectrum with a concentrated aqueous solution of copper sulfate between the sample and detector. No change in the band was observed with or without the filter.

Thus it seems most likely that one or the other of the maxima 18.70 or 19.25 kK is to be associated with a quartet–doublet transition as originally assigned by Jørgensen.[4,13] Therefore, assuming small trigonal splitting, a crystal field calculation in O_h symmetry was performed in an effort to fit the spectrum. The program used, OCTAD37, written by J. C. Hempel, uses symmetry-adapted functions for the $d^{3,7}$ configuration and allows the manual variation of Dq, B, C, and λ. A more complete description of this program appears elsewhere.[43] An attempt to fit the levels $^{2}E_{g}(^{2}G)$, $^{2}T_{1g}(^{2}G)$, $^{4}T_{2g}(F)$, $^{2}T_{2g}(^{2}H)$, $^{4}T_{1g}(^{4}F)$, and $^{2}A_{1g}(^{2}G)$ to the observed features of the spectrum was made. The most reasonable fit of the data appears in Table V. The following assumptions were made to arrive at this result: (1) $Dq \simeq$ 14.5 kK based on the apparent center of gravity of the $^{4}T_{2g}(F)$ manifold; (2) $B \simeq 0.4$ kK based on β values of $Co(dtp)_3$ and $V(dtp)_3$ of 0.38 and 0.43 kK, respectively (Table III); (3) C may be much greater than $4B$ owing to the very low value of B. No reasonable fit of the data (*i.e.*, reasonable parameters) could be obtained by assigning the $^{2}A_{1g}$ level to either the 18.70- or 19.25-kK maximum. Assignment of the $^{2}T_{2g}$ level to either of these maxima and the $^{4}T_{1g}$ to the other gives reasonable values of the parameters and acceptable fit of the data but letting $^{2}T_{2g}$ be the 19.25-kK maximum seems to yield the best overall fit. Introduction of the small trigonal field and spin–orbit coupling effects does not make significant changes in the fit.

TABLE V

CALCULATED AND OBSERVED ENERGY LEVELS IN THE SPECTRUM OF $Cr(dpt)_3$[a]

Excited state	Energy, kK		Excited state	Energy, kK	
	Calcd	Obsd		Calcd	Obsd
$^{2}E_{g}$	12.8	13.1	$^{4}T_{1g}$	18.7	18.75[c]
$^{2}T_{1g}$	13.1	13.6	$^{2}T_{2g}$	19.25	19.25
$^{4}T_{2g}$	14.5	14.5[b]	$^{2}A_{1g}$	25.8	...

[a] Dq = 1.450 kK; B = 0.389 kK; C = 3.260 kK. [b] Center of gravity of ^{4}E and $^{4}A_{1}$. [c] Actually ^{4}E; $^{4}A_{2}$ not observed.

No possible permutation of parameters and assignments seems to offer an explanation for the shoulder at 17 kK. Assignment of this shoulder to the $^{2}T_{2g}$ level places the $^{2}A_{1g}$ 5 kK above the $^{4}T_{1g}$ maximum leaving no acceptable assignment for the extra prominent maximum at 19.25 (or 18.70) kK. Both DeArmond and Schreiner have also observed this weak shoulder at 17 kK in the spectrum of $Cr(dtp)_3$ in absorption[42] and MCD,[44] respectively. However, its origin remains obscure.

The most interesting aspect of the calculation and fit described above and in Table V is the large value of C ($8.4B$). However, this is completely analogous to Jørgensen's analysis of the spectrum in terms of a large β_{55} and small β_{35}.[13] The implication in either case is of much more extensive σ delocalization than π delocalization.

Schreiner[44] has also observed an additional feature in

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(39) D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962).

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(42) K. M. DeArmond, private communication.

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(44) A. F. Schreiner, private communication.

the MCD spectrum of $Cr(dtp)_3$ at 20.38 kK which he associates with the $^2A_1$ level. (No hint of a band at this energy is seen in the absorption spectrum.) Within the limits of the calculation we have made it does not seem possible either to move the $^2A_1$ level near 20.38 kK (without destroying the more certain parts of the fit, *i.e.*, the $^4T_{2g}$ and $^4T_{1g}$ manifolds) or to move the $^2A_{1g}$ and $^4T_{1g}$ levels closer than *ca.* 5 kK to each other. Introduction of a large and (apparently) unlikely second-order trigonal term (v') may suggest new assignments not yet envisioned. More work is in progress on the resolution of this ambiguity. We offer the assignments and parameters of Table V as those which best fit the data at this time.[45]

(45) NOTE ADDED IN PROOF.—Tomlinson has recently published ambient temperature crystal spectra of $Co(dtp)_3$ and $Cr(dtp)_3$ which are in essential agreement with the ambient temperature results reported in this paper [A. A. G. Tomlinson, *J. Chem. Soc. A.*, 1409 (1971)].

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Metal Complexes of Substituted Dithiophosphinic Acids. I. Complexes of Trivalent Chromium

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The preparation and characterization of substituted dithiophosphinate [$S_2PX_2^-$ (X = CF_3, F, CH_3, C_6H_5, and OC_2H_5)] complexes of chromium(III) are described. The magnetic susceptibilities of the Cr(III) complexes over the range 90–303°K follow the Curie–Weiss law with very small Weiss constants. The susceptibilities of the diamagnetic zinc complexes were used to determine diamagnetic corrections for the ligands which for the most part agree with values calculated from Pascal's constants. Other properties of the Cr(III) complexes such as solubility, molecular weights, and mass spectral behavior are consistent with their formulation as six-coordinated, monomeric chelates. The electronic spectra are analyzed in terms of octahedral symmetry. The resultant *Dq* parameters of the ligands decrease in the order F $\sim$ OC_2H_5 > CH_3 $\sim$ CF_3 $\sim$ C_6H_5 with a distinct difference observed between the complexes with F or O bonded to phosphorus as compared to those with P–C bonds and this difference is attributed to π-bonding effects. The complexes show relatively intense spectral bands which can be attributed to the distortion from octahedral symmetry or the presence of substantial covalence in the M–S bonding ($\beta_{35} \cong 0.45$) or more likely both. The infrared spectra of all of the complexes show a strong M–S stretch at 310–320 cm^{-1}.

Introduction

Following the preparation and characterization of the trifluoromethyl-[1,2] and fluorodithiophosphinic[3-5] acids $X_2P(S)SH$ it was of interest to investigate the properties of metal dithiophosphinate complexes which are obtained from the above acids and their salts. For comparison purposes related complexes of dimethyldithiophosphinic, diphenyldithiophosphinic, and bis(*O,O'*diethyl)dithiophosphoric acids have been prepared. We wish to report herein studies of a variety of substituted trivalent chromium complexes[6] of these dithiophosphinic acids. The *O,O'*-dialkyl dithiophosphate complexes $Cr[(RO)_2PS_2]_3$ (particularly the ethoxy derivative) have been known for some time[7,8] and now an extensive series of alkoxy homologs has been investigated.[8] While this paper was in preparation, the synthesis of the $Cr(S_2PF_2)_3$ complex from $F_2P(S)SH$ and chromium metal was also reported;[9] however, spectral[9,10] and magnetic properties[9,10] were only reported in summary. The synthesis of the complex $Cr[S_2P(C_6H_5)_2]_3$ from chromium trichloride and the phenyl acid $(C_6H_5)_2PS_2H$[11,12] and the synthesis and a dipole moment study of $Cr[S_2P(C_2H_5)_2]_3$[13] have been reported. The complexes of the $(C_2H_5)_2PS_2^-$ ligand have been recently reviewed.[14] A brief report of the synthesis of $Cr[S_2PF(C_2H_5)]_3$ along with a listing of the visible absorption bands of this complex has also appeared.[15]

Experimental Part

Volatile air-sensitive compounds, particularly derivatives of the fluoro and trifluoromethyl acids, were handled in a conventional vacuum system, greased with Apiezon N stopcock grease. Other systems could be handled in air or in dryboxes with typical bench-top techniques. Syntheses of $(CF_3)_2PS_2H$[1,2] and F_2PS_2H[3-5] have been described elsewhere.[16]

Infrared spectra were obtained on Perkin-Elmer 421 and Beckman IR-11 instruments. Ultraviolet and visible spectra were measured with a Cary 14 spectrometer; diffuse reflectance

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