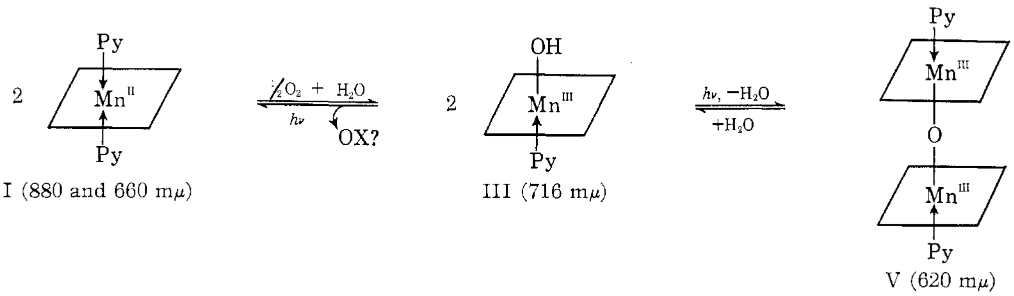
SCHEME II



I (880 and 660 mμ)

III (716 mμ)

V (620 mμ)

manganese(III). Complete spin pairing is unusual for this ion but is possible under two conditions: (a) antiferromagnetic interactions often occur between oxygen-bridged manganese ions; (b) in $Mn^{II}PcPy_2$, the d_{xz},d_{yz} orbitals are the lowest lying of the manganese d orbitals; the manganese has only one unpaired electron, in the d_{xy} orbital.[2] Then we might expect the manganese(III) analog to have its four d electrons paired up in the d_{xz},d_{yz} level.

Still a mystery is the increase in magnetic moment on heating; we should comment that Elvidge and Lever's more drastic heating yielded a product with magnetic moment higher than that of our heated compound, but not yet high enough to correspond to the expected four unpaired electrons. An X-ray structural analysis of these two products would be valuable.

Establishment of the molecular structure of the oxide complex as an oxygen-bridged trivalent manganese compound requires us to revise part of our previously proposed mechanism[1] for the oxidation and reduction reactions of phthalocyaninomanganese. We tentatively propose Scheme II for the reactions of this complex in pyridine solution.

The revised scheme explains reasonably well most but not all of our observations.[1] We suggest that the reaction III → V is a dimerization rather than an oxidation. An absorption peak at about 630 mμ has been reported for the associated species of various complexes of a tetrasulfonated phthalocyanine.[7] However, it is difficult to reconcile this reaction with the apparent disproportionation of the 716-mμ species to the 620- and 660-mμ species. The requirement of air for the photochemical change of the 716- to the 620-mμ species[1] is also puzzling.

To understand the whole picture of the oxidation and reduction reactions, a further study focused on the role and the fate of water in combination with pyridine is required.

Acknowledgments.—This work was supported, in part, by the U. S. Atomic Energy Commission.

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(7) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **44**, 1287 (1961); H. Kobayashi, Y. Torii, and N. Fukada, *Nippon Kagaku Zasshi*, **81**, 694 (1960).

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Ligand Field Theory for Pentacoordinate Molecules. I. The Electronic Spectra of Species with D_{3h} and C_{3v} Symmetry

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Application of the point charge model to the calculation of the energy levels of first-row transition metal ions in ligand fields of D_{3h} symmetry has been made. The results are used to make an assignment of the bands in the electronic spectra of molecules of the types $MX_3 \cdot 2L$ and M(TD)X where L is a unidentate ligand, TD is a tetradentate amine ligand, and X is halogen. Ligand field strengths for the different ligand combinations are calculated and it is shown that to obtain reasonable agreement with the observed spectra, reduction in the interelectron repulsion parameters from their free ion values must be assumed. The amount of reduction for the different ligand combinations follows the same trend as found in complexes of cubic symmetry. While the compounds of formulation M(TD)X do not deviate appreciably from D_{3h} symmetry, it appears qualitatively that better agreement with the observed spectra would be found for a model of C_{3v} symmetry. Some of the band assignments made for these molecules differ from those given previously.

Introduction

The current interest in pentacoordinate molecules of the first-row transition series elements has led to the application of a crystal field model to the interpretation of their spectra.[1] However, apart from the pentachlorocuprate ion, $CuCl_5^{3-}$, for which a molecular orbital study has also been made,[2] none of the molecules considered possesses the symmetries of the two idealized

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(1) (a) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); (b) M. J. Norgett, J. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, *A*, 540 (1967); (c) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

(2) W. E. Hatfield, H. D. Bedon, and S. M. Horner, *Inorg. Chem.*, **4**, 1181 (1965).

pentacoordination polyhedra, *i.e.*, D_{3h} and C_{4v}, for which the calculations were carried out. This is principally because the stoichiometries and/or the constraints provided by chelating ligands prevent them from doing so.

The series of molecules $MX_3 \cdot 2L$ (where M = Ti, V, Cr; X = Cl, Br; L is a unidentate ligand), on the other hand, are capable of attaining the symmetry of the trigonal bipyramid, D_{3h}, and recently investigations of their crystal structures,[3] electronic spectra,[4] and magnetic properties have been carried out. From the first of these, these molecules have been found to be basically trigonal bipyramidal, when L = trimethylamine, with this ligand occupying the axial positions.

While preliminary assignments of the bands in the electronic spectra of these molecules have been made[4] using the results of Nardi, Ciampolini, and Speroni,[5] which are based upon the point dipole approximation with identical ligands, it was felt that they should be particularly amenable to a treatment in which the nonequivalence of axial and equatorial ligand could be accommodated and in which variation of the free-ion interelectron repulsion parameters could be permitted. It is well known from the study of octahedral and tetrahedral molecules that it is necessary to assume a reduction of the interelectron repulsion parameters to fit the observed spectra.

Accordingly, in this study the point charge model was used, in the weak-field approximation, and the crystal field parameters and interelectron repulsion parameters were treated as empirical quantities and adjusted to give the best fit to the observed spectra.

This model has also been extended to a treatment of molecules of C_{3v} symmetry; those prepared by Ciampolini and Nardi[6] from the quadridentate amine tris(2-dimethylaminoethyl)amine being particularly relevant, as the coordination polyhedra in the [Co(Me$_6$tren)Br]Br complex and presumably in the other molecules isomorphous with it are crystallographically required to possess this symmetry.[7]

Further papers will deal with the calculation of energy levels including spin–orbit coupling and the application of ligand field theory to a discussion of the magnetic properties of these molecules.

Theory and Calculations

Calculations of the relative energies of the crystal field states in trigonal-bipyramidal (D_{3h}) symmetry have previously been made, for the d^8 configuration by Ciampolini,[1a] using the point dipole model, and for the d^6, d^7, and d^8 configurations by Norgett, Thornley, and Venanzi,[1b] using tensor operator theory and a point charge model. These latter authors were concerned principally with strong-field, low-spin complexes, so that the crystal field states of interest originate from the free-ion terms of low-spin multiplicity.

1. Notation.—The two independent parameters used to describe the energies of the crystal field states in the field of D_{3h} symmetry have previously been designated Δ_1 and Δ_2, by Allen and Hush,[8] and Q_2 and Q_4 by Norgett, *et al.*[1b] In the present paper we prefer to use the symbols Ds and Dt, thus following the convention recommended by Piper and Carlin,[9] who suggest that crystal field parameters involving differing axial and equatorial terms be denoted as such, irrespective of the symmetry of the field. They are identical with the Δ_2 and Δ_1 but these authors incorrectly assign them to contributions arising solely from axial and equatorial ligands, respectively. With axial and equatorial charges of Z_E and Z_A at distances of a and b, respectively, we define

$$\begin{aligned} Ds &= (1/14)[(4Z_A/b^3) - (3Z_E/a^3)]\bar{r}^2 \\ Dt &= (1/168)[(16Z_A/b^5) + (9Z_E/a^5)]\bar{r}^4 \end{aligned} \qquad (1)$$

so that $Ds = Q_2/14$ and $Dt = (25/168)Q_4$. Since $Dq = Z\bar{r}^4/6R^5$, Dt can be written as $(1/28)(16Dq_A + 9Dq_E)$.

With Ds and Dt defined as above, the one-electron matrix elements within the d manifold and, hence, the real orbital energies are[10]

$$-|0\rangle,\ (z^2),\ a_1',\ 2Ds + 6Dt;\ |\pm1\rangle,\ (xz, yz),\ e'',\ Ds - 4Dt;\ \text{and}\ |\pm2\rangle,\ (xy, x^2 - y^2),\ e',\ -2Ds + Dt \qquad (2)$$

These matrix elements were then used to derive the energies of the triplet and singlet states in the weak-field approximation for the d^2 configuration, and the appropriate triplet and singlet energy matrices were constructed. The coefficients of the single-electron matrix elements in the perturbation matrix for the d^8 configuration, which are identical with those used here, have previously been listed by Ciampolini.[11]

While the relevant energy matrices were solved directly in determining the interelectron repulsion and crystal field parameters, as described in the next section, they were diagonalized for suitable values selected for the parameter Dt and the ratio Ds/Dt to produce the energy level diagrams for the d^2 and d^7 configurations[12] shown in Figures 1 and 2. The free-ion ratios of C/B were used in the construction of these diagrams, and the energy is plotted in units of B with the zero referred to the free-ion ground state.

For the d^7 configuration, the spin multiplicity of the ground state changes at high values of the crystal

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(3) (a) B. J. Russ and J. S. Wood, *Chem. Commun.*, 745 (1966); (b) G. W. A. Fowles, P. T. Greene, and J. S. Wood, *ibid.*, 971 (1967).

(4) M. W. Duckworth, G. W. A. Fowles, and P. T. Greene, *J. Chem. Soc.*, *A*, 1592 (1967). In this paper representative absorption spectra for these systems are illustrated and should be referred to in connection with the discussion to follow.

(5) M. Ciampolini, N. Nardi, and G. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966).

(6) (a) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 1150 (1966); (c) M. Ciampolini, *Chem. Commun.*, 47 (1966).

(7) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967).

(8) G. C. Allen and N. S. Hush, *ibid.*, **6**, 4 (1967).

(9) R. L. Carlin and T. S. Piper, *J. Chem. Phys.*, **33**, 1208 (1960).

(10) The sign convention for Ds and Dt follows that discussed by R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); *i.e.*, positive increases correspond to increased axial fields. The matrix elements are then identical with those listed by these authors, the crystal field potentials having the same form.

(11) See ref 1a. Ciampolini omits the coefficients for the wave functions $(4, \pm1)$ of the ^1G state. These are $^6/_7$, 1, and $^1/_7$ for the matrix elements $\langle 0|V|0\rangle$, $\langle 1|V|1\rangle$, and $\langle 2|V|2\rangle$, respectively. The symmetry of this crystal field state is $^1E''$.

(12) The quartet energy matrices for the d^7 configuration are identical with the triplet energy matrices for d^2.

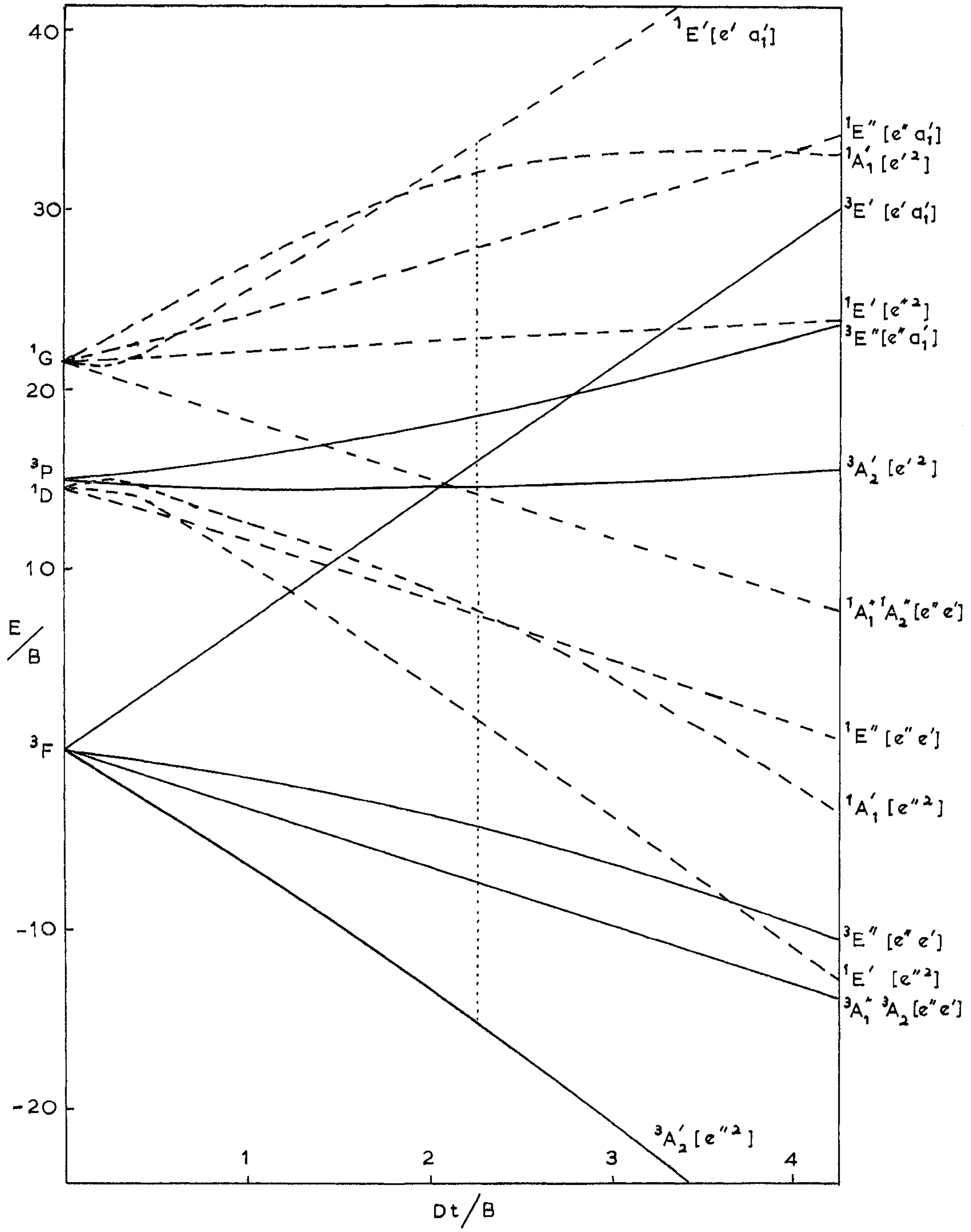

Figure 1.—Energy level diagram for the V(III) ion (d^2) in a crystal field of trigonal-bipyramidal symmetry. The ratio $Ds/Dt = 1/3$ corresponds approximately to the values found for the $VX_3 \cdot 2N(CH_3)_3$ complexes. The diagram is constructed for the free-ion ratio of $C/B = 4.8$ and the dotted line indicates the Dt/B ratio found for $VCl_3 \cdot 2N(CH_3)_3$.

field strength, the $^2E'$ state, arising from the strong-field configuration $e''^4e'^3$, becoming the ground state. Using standard procedures,[13] this strong-field configuration is calculated to have energy $21A - 36B + 18C - 2Ds - 13Dt$, and the transition to the low-multiplicity state occurs when $7Dt + (14/5)Ds > 7B + 4C$.

The splitting pattern of the ^4F and ^4P terms of the d^3 configuration and the ^3F and ^3P terms of the d^8 configuration is inverted with respect to that for d^2 and d^7, and so the weak crystal field ground states are $^4E'$ and $^3E'$, respectively. Here again the multiplicity of the ground state is different for large values of the crystal field parameters and Ciampolini has shown that for d^8 the $^1A_1'$ from the ^1D free-ion term becomes the ground state. The strong-field configuration $e''^4e'^4$ has energy $28A - 38B + 24C - 4Ds - 12\ Dt$ and all spins are paired when $4Ds + 5Dt > 12B + 3C$. For the d^3 configuration the $^2E''$ state arising from ^2G becomes the ground state at high crystal field energies and with a strong-field (e''^3) energy of $3A - 3B + 4C + 3Ds - 12Dt$ the transition to this level occurs when $-3Ds + 5Dt > 12B + 4C$.

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[13] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 76.

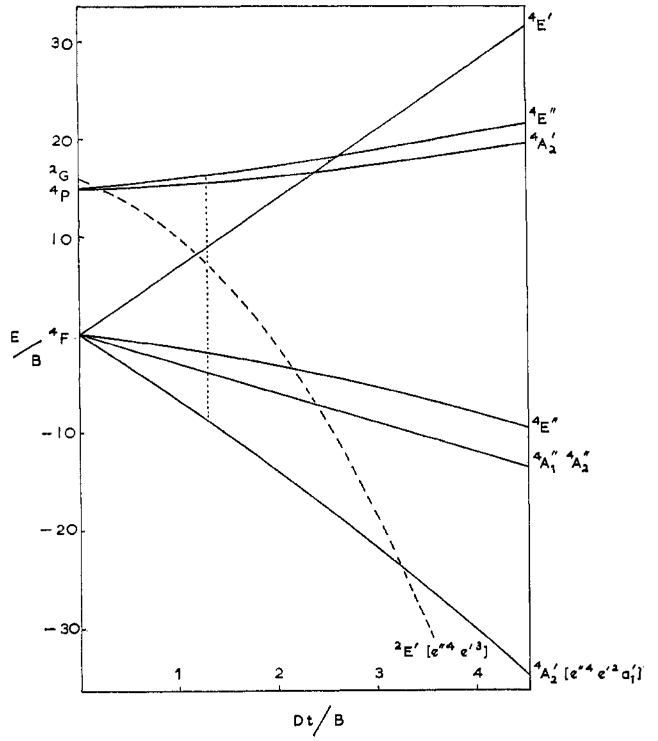

Figure 2.—Energy level diagram for the Co(II) ion (d^7) in a crystal field of trigonal-bipyramidal symmetry constructed with $Ds = 0$ and $C/B = 3.9$. The dotted line indicates the Dt/B ratio found for Co(Me$_6$tren)Cl$^+$.

For the ^{2}D and ^{5}D ground states of the d^9 and d^4 configurations the splitting will be inverted relative to that for these states of the d^1 and d^6 configurations, whose crystal field levels have energies given by (2).

2. **Ligand Fields of C_{3v} Symmetry.**—A point charge model for this symmetry can be derived from the D_{3h} model either by allowing different axial charges, by distortion of the angles (θ) between the axial and equatorial bond directions from 90°, or by a combination of these. The first of these deviations does not cause any change in the form of the crystal field potential so that the energy levels derived for D_{3h} symmetry carry over, the axial contributions in Ds and Dt now being the mean value for the two ligands in question.

Exact quantitative estimation of the energy levels for the various d configurations in the second situation is not practicable in terms of solely Ds and Dt, but it is useful to examine qualitatively the effect of introducing a deviation in the angle θ upon the energy levels. The crystal field potential for this additional perturbation has the form

$$V_\theta = A_2{}^0(9 \cos^2 \theta)(Z_E r^2/a^3) Y_2{}^0 + A_4{}^0(35 \cos^4 \theta - 30 \cos^2 \theta)(3Z_E r^4/a^5) Y_4{}^0 + A_4{}^3 \sin^3 \theta \cos \theta \times (3Z_E r^4/a^5)(Y_4{}^3 + Y_4{}^{-3})$$

where the $A_l{}^m$ are constants, $Y_l{}^m$ are the usual spherical harmonics, and $r < a$. It can be seen that in addition to the introduction of extra quantities into the diagonal elements of the one-electron energy matrix, terms having M_L values differing by 3 now have nonzero matrix elements, so that different D_{3h} representations, belonging to the same representation in C_{3v}, are connected by a parameter dependent on θ and Dt (or Dq). (The potential for D_{3h} symmetry only involves the zeroth-order spherical harmonics $Y_2{}^0$ and $Y_4{}^0$.) The effect of this interaction is, respectively, to lower and to raise the energies of the doubly degenerate e(1) and e(2) levels (previously e″ and e′ in D_{3h} symmetry).

Considering the triplet terms ^{3}F and ^{3}P arising from the d^2 configuration, the matrix elements $\langle \pm 3 | V_\theta | 0 \rangle$ and $\langle \pm 2 | V_\theta | \mp 1 \rangle$ will be nonzero. Inclusion of the first of these leads to a splitting of the previously degenerate $^3A_1''$ and $^3A_2''$ states, for which the wave functions are $(2)^{-1/2}(\langle 3 \rangle + \langle -3 \rangle)$ and $(2)^{-1/2}(\langle 3 \rangle - \langle -3 \rangle)$, respectively. In C_{3v} symmetry, the first wave function transforms as A_2 and can interact with the other states of A_2 symmetry (previously A_2') from the ^{3}F and ^{3}P terms. The other linear combination transforms as A_1 and the energy of the $^3A_1$ state, being the only one of this symmetry, is therefore linear in the crystal field parameters. The second matrix element connects all states of E symmetry so that ^{3}E(2), the ^{3}E′ state in D_{3h} symmetry, is no longer linear in the crystal field parameters. The actual energy of all levels relative to those for the D_{3h} model will depend on the magnitudes of the contributions of V_θ to the diagonal elements, in addition to the off-diagonal elements. However, since these contributions are all small when θ is near 90°, it is reasonable to make initial band assignments using the D_{3h} model.

Results and Discussion

The molecules whose electronic spectra are considered in this paper are adducts of the trihalides of titanium, vanadium, and chromium with trimethylamine and the sulfur ligands, tetrahydrothiophene and dimethyl sulfide, and the complexes formed by the transition metal dihalides (from Cr to Cu) with the quadridentate amine, tris(2-dimethylaminoethyl)amine.[6] The preparation and characterization of the bis-trimethylamine adducts $TiCl_3 \cdot 2N(CH_3)_3$, $TiBr_3 \cdot 2N(CH_3)_3$, $VCl_3 \cdot 2N(CH_3)_3$, $VBr_3 \cdot 2N(CH_3)_3$, and $CrCl_3 \cdot 2N(CH_3)_3$ have been reported elsewhere and their reflectance spectra and solution spectra in several solvents recorded.[4,14] The close similarity of the spectra of the solid vanadium and chromium compounds to their absorption spectra in solution, taken together with a variety of other physical evidence, indicates that these compounds are monomeric and five-coordinate both in the solid and in solution, while X-ray evidence indicates that the titanium analogs are five-coordinate in the solid.[3a]

In contrast, the vanadium complexes $VCl_3 \cdot 2S(CH_3)_2$, $VBr_3 \cdot 2S(CH_3)_2$, $VCl_3 \cdot 2C_4H_8S$, and $VBr_3 \cdot 2C_4H_8S$ are all believed to be dimeric and to contain six-coordinate vanadium in the solid state.[4] Their absorption spectra in benzene solution, however, show marked similarity to those of the trimethylamine adducts, both with regard to positions and to relative

[14] G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, 33 (1963).

Table I

Observed and Calculated Band Energies for Complexes $VX_3 \cdot 2L$ (in cm^{-1})

Transition	$VCl_3 \cdot 2N(CH_3)_3$		$VBr_3 \cdot 2N(CH_3)_3$		$VCl_3 \cdot 2(CH_3)_2S$[c]		$VBr_3 \cdot 2(CH_3)_2S$[c]	
	Obsd[a]	Calcd[b]	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$^3A_2' \rightarrow {}^3A_1'' + {}^3A_2''$	4,800 (60)	4,800	4,200	4,250	5,500 (53)	5,500	4,700 (50)	4,700
$\rightarrow {}^3E''$	7,000 (16)	6,950	6,050 (14)	6,120	7,050 (13)	6,970	6,400	6,300
$\rightarrow {}^1E'(D)$		10,400		9,900				
$\rightarrow {}^1A_2'(D)$?	12,700 w		12,600 (6)		12,200 (5)		12,300 w	
$\rightarrow {}^1E''(D)$	16,600 (10)	16,520	14,600 (7)	14,500				
$\rightarrow {}^3E'$	19,700 (60)	19,700	18,400 (66)	18,400	18,500 (51)	18,500	18,100 (52)	17,700
$\rightarrow {}^3A_2'(P)$	[19,700]	19,300	[18,400]	16,750	[18,500]	18,400	[18,100]	16,200
$\rightarrow {}^3E''(P)$	[19,700]	21,450	[18,400]	19,500	[18,500]	17,400	[18,100]	18,000

[a] ϵ_{max} values in parentheses. [b] Calculated from the crystal field parameters in Table III. [c] The spectra of the tetrahydrothiophene complexes are very similar.

intensities of the bands, and so these, too, can be assigned a five-coordinate structure in solution.[4]

The energies of the band maxima and their molar extinction coefficients are listed in Table I, together with the values calculated as described below. Only the solution spectra data are quoted here, the bands being of a higher resolution than in the reflectance spectra, and average experimental values are given where the spectra in several solvents were obtained.

The shapes of the absorption bands call for comment. The second low-energy band (in the range 6000–7000 cm^{-1}) in the spectra of the vanadium complexes is markedly asymmetric,[4] and it is probable that the band envelope contains more than one transition. Likewise, the highest energy band, at ~19,000 cm^{-1} in the vanadium complexes, and the band at 17,600 cm^{-1} in $CrCl_3 \cdot 2N(CH_3)_3$ are very broad and comprise several transitions.

The electronic spectra of the series of molecules $[M(Me_6tren)X]X$ have been reported by Ciampolini and Nardi[6] and their data for the solution spectra absorption band maxima have been used in these calculations.

1. Compounds of Type $MX_3 \cdot 2L$.—Considering first the bis-trimethylamine vanadium trihalide complexes and referring to Figure 1, we can assign the bands at 4800 and 7000 cm^{-1} in the chloride complex and at 4200 and 6000 cm^{-1} in the bromide complex to the transitions $^3A_2' \rightarrow {}^3A_1''$, $^3A_2''$ (ν_1) and $^3A_2' \rightarrow {}^3E''$ (ν_2), and their relative intensities as measured by their ϵ_{max} values are consistent with this assignment, ν_1 being allowed by the electric dipole selection rules if d–p mixing is taken into consideration. In considering the transition $^3A_2' \rightarrow {}^3E'$, which is also dipole allowed, the shoulders at 16,500 cm^{-1} in the chloride and at 14,700 cm^{-1} in the bromide appear too weak to be so assigned, and therefore the maxima of the broad bands at 19,700 and 18,400 cm^{-1}, respectively, are taken as a measure of the energy of this transition. Using this value for ν_3, together with the value for ν_1, the value of the Racah parameter, B, was adjusted until the calculated value for the ν_2 transition gave good agreement with that observed. From the values of the parameters Ds, Dt, and B so derived, the positions of the transitions $^3A_2' \rightarrow {}^3A_2'(P)$ and $^3A_2' \rightarrow {}^3E''(P)$ were calculated and for both the chloride and bromide complexes are found to lie within the broad band envelope whose maximum was taken as ν_3. The values for Ds, Dt, and B are listed in Table III.

There thus remain the weaker bands at 16,600 and 14,700 cm^{-1} and the shoulders on the high-energy side of the ν_2 bands. These are assigned to the (formally) spin-forbidden transitions $^3A_2' \rightarrow {}^1E''(D)$ and $^3A_2' \rightarrow {}^1E'(D)$, respectively, although their ϵ_{max} values are relatively high. However, it is likely that, being situated near spin-allowed transitions, they "steal" intensity by spin–orbit coupling. As a check on this assignment the predicted transition energies were calculated by diagonalizing the appropriate singlet energy matrices. Assuming the free-ion value of 4.8 for the ratio of the Racah parameters, C/B, the calculated energies of these two transitions are given, along with the calculated values for the spin-allowed transitions, in Table I and the agreement for $^3A_2' \rightarrow {}^1E''(D)$ is excellent for both the chloride and bromide complexes.

Turning to the two titanium complexes $TiCl_3 \cdot 2N(CH_3)_3$ and $TiBr_3 \cdot 2N(CH_3)_3$, we might anticipate values of Dt and Ds very similar to (or perhaps slightly higher than) those found for the vanadium analogs. The predicted energies of the $^2E'' \rightarrow {}^2A_1'$ transition ($10Dt + Ds$) for the two species, assuming the same values, are then 14,940 and 13,920 cm^{-1}, respectively, in very good agreement with the values of 15,000 and 14,000 cm^{-1} obtained for the single symmetrical peak in the diffuse reflectance spectra of the two compounds.[15] The predicted energies of the two $^2E'' \rightarrow {}^2E'$ transitions ($-3Ds + 5Dt$) are 5930 and 5140 cm^{-1}, respectively.[15a]

Considering the spectrum of the chromium complex $CrCl_3 \cdot 2N(CH_3)_3$, the first band at 10,000 cm^{-1} (23) can be assigned to the (weakly) dipole-allowed transition $^4E' \rightarrow {}^4E''$ (ν_1), while the remaining broad, strong band at 17,600 cm^{-1} (130) probably accommodates the three dipole-allowed transitions $^4E' \rightarrow {}^4A_2'$ (ν_3),

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(15) T. E. Lester, University of Reading, private communication. Reference 14 gives a value 15,380 cm^{-1} for $TiCl_3 \cdot 2N(CH_3)_3$, derived from reflectance measurements, while for trimethylamine solution the values are 14,900 and 14,200 cm^{-1} for the chloride and bromide, respectively. However, the possibility of solvation occurring giving a six-coordinate species in solution cannot be ruled out for these systems.

(15a) Note Added in Proof.—Examination of the reflectance and trimethylamine solution spectra in the region down to 5000 cm^{-1} has confirmed these estimates for $TiCl_3 \cdot 2N(CH_3)_3$ (G. W. A. Fowles, private communication). The $^2E'' \rightarrow {}^2E'$ transition occurs at 6200 cm^{-1} and is much more intense than the $^2E'' \rightarrow {}^2A_1'$ transition, consistent with it being dipole allowed. Ds and Dt are accordingly estimated as 340 and 1470 cm^{-1}, respectively. The close similarity of the spectrum in solution to that in the solid indicates the maintenance of a five-coordinate structure in trimethylamine.

TABLE II

OBSERVED[6] AND CALCULATED BAND ENERGIES IN [Co(Me$_6$tren)X]X COMPLEXES (IN CM^{-1})

	X = Cl		X = Br		X = I		X = ClO$_4$	
Transition	Obsd[a]	Calcd[b]	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$^4A_2' \rightarrow {}^4A_2'' + {}^4A_1''^c$ (ν_1)		4,260		4,000		4,000		4,300
$\rightarrow {}^4E''$ (ν_2)	5,800 (32)	5,750	5,700 (30)	5,600	5,600 (37)	5,400	5,900 (22)	5,900
$\rightarrow {}^2E'(G)$	12,600 (30)		12,300 (29)		12,100 (16)		13,500 (23)	
	15,500		15,600				15,900	
$\rightarrow {}^4E'^c$ (ν_3)	} (87)	14,800	} (128)	14,050	16,100 (198)	13,900	} (47)	14,700
	16,100		16,000				16,400	
$\rightarrow {}^4A_2'(P)$ (ν_4)	20,500	20,680	19,800	19,800	19,300	19,200		21,200
	} (188)		} (112)		} (199)		20,600 (82)	
$\rightarrow {}^4E''(P)$ (ν_5)	19,800	19,700	19,200	19,000	18,600	18,500		20,400

[a] ϵ_{max} values in parentheses. [b] Calculated using the values listed in Table III. [c] The transitions which are dipole allowed in D_{3h} symmetry. All transitions are weakly allowed in C_{3v} symmetry except $^4A_2 \rightarrow {}^4A_1$ ($^4A_2''$).

$^4E' \rightarrow {}^4E''(P)$ (ν_4), and $^4E' \rightarrow {}^4A_2'(P)$ (ν_5). The weak band at 13,000 cm^{-1} can then be assigned to the dipole-forbidden transition $^4E' \rightarrow {}^4A_1''$, $^4A_2''$ (ν_2). However, the agreement between the observed band energies and their values calculated using crystal field parameters roughly similar to those found for the vanadium analogs and a B value reduced to ~80% of its free-ion value is poor, and it must be concluded that the observed distortion of the coordination polyhedron from D_{3h} symmetry, in the crystal[3] (and also presumably in solution because of the near identity of the spectra), is sufficient to make an assignment of bands using this model unrealistic. The calculated energies for the transitions ν_1 through ν_5, assuming Ds = 400 cm^{-1}, Dt = 1450 cm^{-1}, and B = 800 cm^{-1} (free-ion value 1040 cm^{-1}) are 9770, 15,900, 15,500, 23,200, and 26,300 cm^{-1}, respectively, while, in addition to the three bands mentioned above, the only other observed (potentially ligand field) band is a weak one at 23,200 cm^{-1}.

The assignment of bands and calculation of crystal field parameters for the bis(dimethyl sulfide)- and bis(tetrahydrothiophene)vanadium trihalide complexes follows the same pattern as for the trimethylamine complexes. The peak positions for the two compounds with the same halide ligand are very similar and one set of parameters suffices to explain both spectra. The calculated energies are tabulated in Table I, along with the observed values for the dimethyl sufide complexes.

2. Compounds of Type [M(Me$_6$tren)X]X.—The assignments of bands in the spectra of these compounds have been made by Ciampolini, *et al.*,[5] on the basis of point dipole calculations, with all ligands equivalent. However, assignment using the energy matrices developed here leads to some important differences.

Considering the spectra of the cobalt complexes, the two strong bands in [Co(Me$_6$tren)Cl]Cl are assigned by Ciampolini, *et al.*,[5] to the $^4A_2' \rightarrow {}^4A_2'(P)$ (ν_4) and $^4A_2' \rightarrow {}^4E''(P)$ (ν_5) transitions, while the much weaker peak at 12,500 cm^{-1} they assign to the ν_3 transition $^4A_2' \rightarrow {}^4E'$ which is (weakly) dipole-allowed in D_{3h} symmetry if p and d mixing is taken into account. In view of the discrepancy in intensities and moreover the observed splitting of the band at ~15,900 cm^{-1} into two components, which is not easily accounted for in this assignment, we prefer to assign this to the ν_3 transition, and the band at 20,000 cm^{-1}, which has a distinct shoulder on the high-energy side, to the ν_4 and ν_5 transitions. The observed splitting of the 15,900-cm^{-1} band can then be attributed to spin–orbit coupling, and the magnitude of the energy separation of the two components, 500 cm^{-1}, is perfectly reasonable. (The components of the $^4E'$ level including spin–orbit coupling have energies $\pm 3\lambda$ and $\pm\lambda$.) Assigning the peak at 5800 cm^{-1} to the ν_2 transition, there remains the origin of the peak at 12,500 cm^{-1}. Although this has an ϵ_{max} of 30 we believe it can be assigned to the transition $^4A_2' \rightarrow {}^2E'(G)$ which becomes weakly spin allowed and also hence weakly dipole allowed, on inclusion of spin–orbit coupling. Moreover, its close proximity to the ν_3 band (see Figure 2) means that it can acquire intensity by coupling with this transition.

With the above assignment, the relevant energy matrices were used to derive values for Ds, Dt, and B, and the results are given in Table III. The calculated value for the energy of ν_3 is somewhat lower than observed, but, when it is noted that the $^4A_2$ ground state in C_{3v} symmetry will probably lie at lower energy, owing to the interaction with the other $^4A_2(F)$ state, this can be accounted for. The observed and calculated transition energies for the cobalt complexes studied are listed in Table II and Figure 2 gives an energy level diagram constructed for Ds = 0.

Stronger evidence for the use of a C_{3v} model is provided by the analogous nickel complexes whose solution spectra all show a double-peaked band in the region of 11,000 cm^{-1}, the splitting being ~500 cm^{-1}. While in D_{3h} symmetry this can be assigned to the ν_2 transition $^3E' \rightarrow {}^3A_1''$, $^3A_2''$ for the reasons mentioned earlier, these states are no longer degenerate in C_{3v} symmetry and so this prediction appears to be experimentally confirmed. The assignment in D_{3h} symmetry follows the same pattern, apart from some minor differences, as that given by Ciampolini and coworkers.[5] However, the calculated energies of the five spin-allowed transitions and in particular ν_3, using crystal field parameters derived, do not agree too well with the observed values. Since the peak positions are roughly the same for all three halide complexes, Ni(Me$_6$tren)X$^+$, parameters were derived solely for the chloride complex, as those for the bromide and iodide complexes will be little different. The observed and calculated values for this chloride complex, with ϵ_{max} values in parentheses, are: ν_1: 7100 (28),

Table III

Ligand Field Parameters for Five-Coordinate Complexes (in cm^{-1})

Compound	Ds	Dt	B^a	β^b	Dq_{eq}	Dq_{ax}
$VCl_3 \cdot 2N(CH_3)_3$	440	1450	650	0.75	1790	1530
$VBr_3 \cdot 2N(CH_3)_3$	520	1340	550	0.64	1640	1420
$VCl_3 \cdot 2(CH_3)_2S$	−100	1260	500	0.57	1790	1200
$VBr_3 \cdot 2(CH_3)_2S$	150	1285	450	0.53	1640	1330
$Co(Me_6tren)Cl^+$	−100	1040	810	0.73		
$Co(Me_6tren)Br^+$	−50	1000	790	0.71		
$Co(Me_6tren)I^+$	−50	980	750	0.67		
$Co(Me_6tren)ClO_4^+$	−65	1070	840	0.76		
$Ni(Me_6tren)Cl^+$	100	1070	830	0.77		

[a] The free-ion values of B for V^{3+} and Co^{2+} are 860 and 1120 cm^{-1}, respectively. [b] $\beta = B(\text{complexed ion})/B(\text{free ion})$.

7800 cm^{-1}; ν_2: 10,900–11,600 (22), 10,800 cm^{-1}; ν_3: 14,900 (30), 12,000 cm^{-1}; ν_4: 20,600, 20,530 cm^{-1}; ν_5; 23,500 (172), 22,300 cm^{-1}. The derived crystal field parameters are given in Table III.

The spectra of the chromium, iron, and copper analogs show essentially one band in the region of 10,000–12,000 cm^{-1}, and this can, in the case of the iron complexes, be assigned to the transition $^5E(1) \rightarrow {}^5A_1$, in C_{3v} symmetry. Using the values of Dt and Ds derived for the corresponding cobalt complexes, the calculated values of 10,300 and 9950 cm^{-1} are seen to be in good agreement with the values of 10,500[5] and 9800 cm^{-1}[6b] observed for the chloride and bromide complexes, respectively, and the predicted value for the $^5E(1) \rightarrow {}^5E(2)$ $(4Ds + 5Dt)$ transition is 4800 cm^{-1} compared with *ca.* 4500 cm^{-1} observed for the bromide.

The band in the chromium and copper complexes is very broad and shows considerable splitting in the solution spectra, of the order of 3000 cm^{-1}. Accordingly the two components of the band in each instance were assigned to the two transitions $^{2(5)}A_1' \rightarrow {}^{2(5)}E(1)$ and $^{2(5)}A_1' \rightarrow {}^{2(5)}E(2)$.[6] However, it would appear from the relative magnitudes of Ds and Dt for the cobalt complexes, and also from the relative energies of the two transitions in the corresponding iron complexes, that the second transition should occur at much lower energies and that the observed splitting must have some other origin. These conclusions are, of course, strongly dependent on the relative values of Ds and Dt which were derived for the D_{3h} model. Inclusion of the additional terms in the C_{3v} model may alter these conclusions.[16]

3. Analysis of the Estimated Ligand Field Parameters.—From the values of B and Dt, tabulated for the vanadium and cobalt complexes in Table III, it can be seen that the changes in these parameters for the different ligand combinations parallel those found for Dq and B in octahedral and tetrahedral systems. Thus we find that, for the vanadium complexes, the combination of chloride and trimethylamine ligands has the largest ligand field strength, as would be anticipated from their positions in the spectrochemical series, relative to Br^- and the sulfur ligands, and that the largest reduction in B is shown by the sulfur adducts, again in accord with the position of this type of ligand in the nephelauxetic series.

A similar trend is found in the parameters for the series of $Co(Me_6tren)X^+$ species although, since they were derived for a D_{3h} model, their actual numerical values will not be so reliable. However, it does appear from these two groups of results that the values of Dt for trivalent ions are consistently higher than for divalent ions, in common with the situation for cubic complexes.

The use of the relationship between Dt and the Dq values for the different ligands allows calculation of the field strength of one ligand, if that for the second is known, provided due allowance is made for variation of metal ligand distances and provided the mean radius term $(\bar{r}^4)$ remains constant.

Since data on Dq values for Ti, V, and Cr are available from studies of the hexahalometalates,[17] it is feasible to compare the strengths of axial and equatorial fields in the vanadium species. The values of Dq for Cl^- and Br^- in TiX_6^{3-} are 1190 and 1180 cm^{-1}, and in VX_6^{3-}, 1242 and 1190 cm^{-1}. However, these values are anomalously low owing to the probable long metal–halogen bond in these species and must be adjusted. Since no bond-length data exist, we may estimate values based on steric considerations of the packing of the six halide ions around the metal (assuming octahedral coordination), and, for the relevant M–Cl and M–Br distances, approximate values of 2.4 and 2.6 Å are obtained, compared with the observed values of 2.23 Å in $CrCl_3 \cdot 2N(CH_3)_3$[3b] and 2.43 Å in $TiBr_3 \cdot 2N(CH_3)_3$.[3a] Taking the vanadium–halogen distances to be the same, the values Dq_{eq} and Dq_{ax} were derived and are listed in Table III. While these results can only be very approximate, they do suggest that the axial ligand fields in these molecules are weaker than those arising from the equatorial halide ligands, and in the case of the $N(CH_3)_3$ adducts this is consistent with the rather long metal–nitrogen bonds found in these molecules.[3] The lower estimated field strengths in the sulfur complexes are also consistent with the lower values of Ds, which involve a weighted *difference* of the two contributions, observed for these molecules.

The values of Ds for the cobalt complexes also indicate a much weaker axial field present in these molecules and this is consistent when the nature of the ligands is considered, since the equatorial nitrogen atoms would be expected to provide a contribution similar to ethylenediamine, while the Dq values for tertiary nitrogen and halogen will be smaller.

The poor agreement between observed and calculated energies for $CrCl_3 \cdot 2N(CH_3)_3$ is almost certainly due to the presence of a large low-symmetry ligand field component operative in this molecule, which (ne-

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(16) A similar splitting of the band at ~9000 cm^{-1} in the spectrum of the $CuCl_5^{3-}$ ion is observed and the same ambiguity as to its assignment exists.[1c,8] From the anticipated relative magnitudes of Ds and Dt, it appears that the two components are more likely to be the result of spin–orbit coupling and the operation of a Jahn–Teller effect in the excited $^2E''$ state.

(17) B. J. Russ and G. W. A. Fowles, *J. Chem. Soc., A*, 517 (1967); B. J. Russ, Ph.D. Thesis, Southampton University.

glecting spin–orbit coupling) has a $^4E'$ ground state. Such an orbitally degenerate ground state ($^3E'$) exists for the nickel complex $Ni(Me_6tren)Cl^+$, and, while the poor agreement in calculated and observed transition energies may be partially offset by use of a C_{3v} model, there might be distortion (in addition to spin–orbit coupling) tending to remove the orbital degeneracy, although the probable presence of threefold symmetry for the molecule in the solid would seem to refute this.[7] The agreement using the point dipole model in fact appears to be much better,[5] although the difference between the two values of μ (1.2 and 2.2 au), at which the "best fit" is achieved for the cobalt and nickel complexes, appears to be unrealistic.

Detailed studies of the magnetic properties of all of the trimethylamine adducts over a temperature range have indicated[18] that, in addition to $CrCl_3 \cdot 2N(CH_3)_3$, additional low-symmetry ligand field components are also operative in the titanium analogs and that these are presumably necessary (in addition to spin–orbit coupling) to remove the orbital degeneracy of the ground state; while for the vanadium complexes, the magnetic properties are consistent with maintenance of D_{3h} symmetry as would be anticipated for the $^3A_2'$ ground term. The magnitude of the low-symmetry component has been estimated in the case of the titanium complexes and the fact that it is much smaller (as indicated by the magnetic data) than in the chromium complex is consistent with the measured distortions from D_{3h} symmetry found by X-ray analysis.[3] This difference in degree of distortion is apparently reflected in the poor agreement achieved for $CrCl_3 \cdot 2N(CH_3)_3$ with the chosen values of Ds and Dt, while the agreement for the titanium species is satisfactory.

Similar magnetic studies on the nickel complex mentioned above would provide more definitive information on the nature of the ground state, since these properties are much more sensitive to small distortions than are spectra.

4. Complexes of Low-Spin-Multiplicity Ground States.—The species discussed thus far all have crystal field parameters much less than would be necessary to produce low-spin complexes as given by the conditions listed earlier; *e.g.*, the critical value of $5Dt - 3Ds$ for d^3 would be *ca.* 25,000 cm^{-1}. However, while $CrCl_3 \cdot 2N(CH_3)_3$ is the only pentacoordinate molecule of chromium(III) known, a variety of low-spin pentacoordinate molecules of Co(II) and Ni(II) have recently been synthesized, and so presumably the left-hand side of the relevant inequality is the larger in these instances.[19] These species all contain ligands, such as substituted phosphines and arsines, which can participate in extensive π bonding with the metal. This latter leads to increased values of Dt and to decreased values of the interelectron repulsion parameters, so it would be anticipated that the spectra, the bands of which are much more intense than those dealt with here, would be best considered on a molecular orbital scheme. However, a crystal field model has been applied to these systems with apparent success.[1b]

Conclusions

From the foregoing results and discussion, the usefulness of a ligand field model in the interpretation of the spectra of a variety of basically trigonal-bipyramidal pentacoordinate molecules has been demonstrated. Treating ligand field and interelectron repulsion parameters as adjustable variables, good agreement with experiment is obtained for those molecules conforming closely to D_{3h} symmetry, while the agreement is only fair for molecules with lower symmetry. Moreover, the deviation from D_{3h} symmetry apparently does not need to be large to make calculated values of ligand field parameters unrealistic, within their context, so that care needs to be taken with assignments of bands, when the model on which they are based is a poor approximation. The features characteristic in the interpretation of the spectra of cubic complexes, *i.e.*, reduction of Racah parameters, relative magnitudes of ligand field strengths, etc., all seem to apply equally well in the spectra of pentacoordinate molecules.

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(18) P. T. Greene and J. S. Wood, submitted for publication.

(19) See, for example: G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967), and references therein; L. M. Venanzi, *Angew. Chem. Intern. Ed., Engl.*, **3**, 453 (1964).