CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YORK UNIVERSITY,
DOWNSVIEW, ONTARIO, CANADA

The Electronic Spectra of Linear Transition Metal Dihalides. A Theoretical Approach Involving Ground-State-Energy Space Diagrams

BY A. B. P. LEVER* AND B. R. HOLLEBONE

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The electronic spectra of the linear transition metal dihalides are interpreted in terms of the "orbital angular overlap" model. Ground-state-energy space diagrams are constructed, which illustrate the various possible ground terms for a linear d^n species and by consideration of the chemistry of the species enable a choice of the most probable ground term to be made. Semiempirical molecular-orbital parameters are calculated from the data considering all possible assignments, and a set chosen which are internally consistent with the electronic configurations of the various d^n species. It is probable that a donor-π interaction between the halogen and the metal is very important in many of these species.

The electronic spectra of gaseous phase and matrix-isolated transition metal dihalides (MX_2, where M = V(II), Cr(II), Fe(II), Co(II), Ni(II), and Cu(II), and X = Cl, and in certain cases Br and I) have been extensively studied.[1-7] Controversy has been rife concerning the assignments pertinent to these complexes and with attempts to fit the band energies to various theoretical models.[1-3,8,9] A qualitative treatment of the ultraviolet spectra of these species has been reported,[4] as have quantitative studies of cobalt chloride[7] and nickel chloride[8] inclusive of spin-orbit coupling. However, even at this time none of the assignments can be regarded as definitive because of the lack of independent corroboration. Unfortunately because of the nature of these species, polarized single-crystal studies cannot be undertaken as a means of such independent corroboration.

In this paper all possible assignments are considered in the light of the various theoretical models and a consistent set of assignments is sought.

Experimental Section

All experimental band energies were obtained from the literature. The data, using only three variables (see below), were fitted to the secular determinants by an iterative program written in WATFIV and run on an IBM 360/50 computer.

Results and Discussion

Written in Racah's rationalized harmonics, the crystal-field potential for a linear molecule may readily be shown to be (excluding spherical term)

$$H = 2Ze(\overline{r^2}/S^3)C_2^0 + 2Ze(\overline{r^4}/S^5)C_4^0 \qquad (1)$$

where S is the metal-ligand distance and the other terms have their usual significance. If the crystal-field radial integrals Ds and Dq are defined as

$$Ds = -(6Ze/7)(\overline{r^2}/S^3) \qquad (2)$$

$$Dq = (Ze/6)(\overline{r^4}/S^5) \qquad (3)$$

then the Hamiltonian becomes

$$H = -(7/3)DsC_2^0 + 12DqC_4^0 \qquad (4)$$

The definitions of Ds and Dq are those previously used in connection with trigonally distorted complexes[10] since a linear molecule may be derived from an octahedral molecule by compression along the threefold axis until the angle between this axis and the bonding axes becomes zero ($\alpha = 0$[10]). The Hamiltonian (4) may be directly obtained from the trigonal-field Hamiltonian (eq 5, ref 10) by writing $\alpha = 0$ and dividing by 3 since there are now two ligands rather than six. The advantage of this model is that the values of Dq and Ds obtained may be directly compared against those found for octahedral or trigonally distorted octahedral molecules.

There is also a direct correlation with our previous discussion of tetragonally distorted complexes.[11] Linear molecules may be assumed to arise from tetragonal derivatives MX_4Z_2 by removing the equatorial (X) ligands to infinity. Linear MZ_2 molecules are related therefore to this previous discussion by writing $R = \infty$ (equatorial metal-ligand bond distance) and $A = 1$ (anisotropic mean charge ratio).[11] Under such circumstances the distinction between Dq and Dt disappears. Linear molecules are therefore special cases of the stereochemistries previously discussed.[10,11]

Ds and Dq are related to the previously defined[1] A_2 and A_4 radial integrals by the expressions

$$Ds = -6A_2 \qquad Dq = 7A_4/2 \qquad (5)$$

Following our previous discussion[10] it is convenient to discuss these data in terms of the ratio $\overline{r^2}/\overline{r^4}$, designated G, which gives a direct measure of the ratio of the second- and fourth-order contributions to the field. Setting R^2 arbitrarily as 4, then

$$G = -7Ds/144Dq \qquad (6)$$

and *the energy levels may be described by the variables G and Dq, and, where relevant, B the Racah parameter.*

Before considering the energy levels arising from this Hamiltonian it is convenient to pursue a relationship between this crystal-field model and the orbital angular

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(1) J. T. Hougen, G. E. Leroi, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).

(2) C. W. DeKock and D. M. Gruen, *ibid.*, **44**, 4387 (1966).

(3) C. W. DeKock and D. M. Gruen, *ibid.*, **46**, 1096 (1967).

(4) C. W. DeKock and D. M. Gruen, *ibid.*, **49**, 4521 (1968).

(5) D. E. Milligan, M. E. Jacox, and J. D. McKinley, *ibid.*, **42**, 902 (1965).

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(8) C. K. Jørgensen, *Mol. Phys.*, **7**, 417 (1964).

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(10) A. B. P. Lever and B. R. Hollebone, *J. Amer. Chem. Soc.*, **94**, 1816 (1972).

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overlap model.[12-18] In this model the one-electron energies of the d orbitals relative to the low-lying δ orbitals set at zero are given by[15,18]

$$\begin{aligned} &(\sigma) \quad z^2 = 2e'_\sigma = -4Ds/3 + 20Dq/7 \\ &(\pi) \quad xz, yz = 2e'_\pi = -Ds - 20Dq/7 \\ &(\delta) \quad x^2 - y^2, xy = 0 \end{aligned} \tag{7}$$

where the crystal-field energies derived from the Hamiltonian (4) are also cited. The e'_σ and e'_π parameters[18] purport to measure directly the σ- or π-bonding or antibonding nature of the metal orbitals concerned. They have the special utility of, in principle, being transferable from one complex to another. While such parameters have a specific mathematical significance, their chemical significance is still unproven.

Indeed one of the purposes of this paper is to ascertain whether the numerical values of these parameters, as derived from spectroscopic measurements, really do provide chemical information regarding the relative importance of σ and π bonding in metal complexes.[15,17,19]

Rearrangement of (7) leads to

$$\begin{aligned} Ds &= (-6/7)(e'_\sigma + e_\pi') \\ 10Dq &= 3e'_\sigma - 4e'_\pi \end{aligned} \tag{8}$$

The σ^* and π^* parameters[12] used by Smith[9] are related to these parameters by a simple factor.

(i) **Energy Levels.**—Using standard techniques[11,20,21] the energies of all spin-allowed transitions within the various d^n manifolds can be readily deduced. Thus eq 7 can be used directly to calculate the transition energies within the Δ_g, Π_g, and $\Sigma_g{}^+$ states of d^1 and d^6, while the transitions within d^4 and d^9 can be obtained from eq 7 by multiplying by -1 and rearranging to set $\Sigma_g{}^+$ as the ground term (see below), *viz.*

$$\begin{aligned} E(\Delta_g) &= -4Ds/3 + 20Dq/7 \\ E(\Pi_g) &= -Ds/3 + 40Dq/7 \\ E(\Sigma_g{}^+) &= 0 \end{aligned} \tag{9}$$

For d^2 (and d^7) the energies relative to the unsplit F term as zero and the relationship between the group theoretical terms and the $|L, M_L\rangle$ functions are given in Chart I.

The relative energies for the terms from d^3 and d^8 may be obtained from Chart I by multiplying the coefficient of Ds and Dq (but not B) by -1. This procedure has the advantage that the same definitions of Ds and Dq (eq 3) are retained for all d^n configurations.

CHART I

$$\Phi_g = |3, \pm 3\rangle = Ds/3 - 12Dq/7$$

$$\Delta_g = |3, \pm 2\rangle = 4Dq$$

$$\Pi_g$$

$$\begin{array}{lll} & |3, \pm 1\rangle & |1, \pm 1\rangle \\ |3, \pm 1\rangle & -Ds/5 - 4Dq/7 - E & 4(2/3)^{1/2}Ds/5 - 4(6)^{1/2}Dq/7 \\ |1, \pm 1\rangle & & -7Ds/15 + 15B - E \end{array}$$

$$\Sigma_g{}^-$$

$$\begin{array}{lll} & |3, 0\rangle & |1, 0\rangle \\ |3, 0\rangle & -4Ds/15 - 24Dq/7 - E & -4Ds/5 - 16Dq/7 \\ |1, 0\rangle & & 14Ds/15 + 15B - E \end{array}$$

(ii) **Sign of Dq and Ds.**—Using the definition in (3) and given that all quantities involved in the definition of Dq are inherently positive, Dq is always positive in this model. By similar arguments Ds is seen to be always negative. However, these conclusions assume that the crystal-field model is relevant and that the definitions (3) do adequately represent Dq and Ds. If the orbital angular overlap model is considered, then the definitions (8) apply. The quantity e'_σ is positive since all ligands are σ donors. The quantity e'_π is positive for a π-donating ligand and negative for a π-accepting ligand. Thus Ds will be negative unless there is interaction with a ligand whose π-accepting ability exceeds its σ-donor ability. This situation, while not impossible, will surely not prevail with the halogen ligands. Since the σ-donor ability of a ligand will always exceed its π-donor ability, by virtue of the nature of σ and π bonding, Dq will be positive unless the π-donor ability, as measured by e'_π, exceeds 75% of e'_σ, an unlikely, but perhaps not impossible, event.

(iii) **Range of Existence of Dq.**—For the metal ions under consideration Dq for octahedrally coordinated halogen species is of the order of 700–1000 cm^{-1}. While the Dq for the corresponding tetrahedral species would be of the order of four-ninths of this amount, it would be erroneous to assume that the Dq values for linear two-coordinate molecules would be even smaller. The "non sequitur" arises from the definition of Dq employed here. As defined by eq 3, Dq is independent of the coordination number or stereochemistry. The direct relationship, alluded to above, between these linear systems and the "octahedral" complexes previously discussed[10,11] infers that if the values of Z, $\overline{r^4}$, and S remain unchanged from their octahedral values, Dq would lie in a similar range. In fact S, the metal–ligand distance, may be expected to be smaller in the linear molecules than in the octahedral molecules, thereby increasing Dq. However, it is not obvious how Z and $\overline{r^4}$ will change; certainly high values of Dq should not be unexpected. Using definition (8), increases in both e'_σ and e'_π might be expected when compared with their octahedral values, and a decrease in Dq may be plausible.

(iv) **Sign and Magnitude of $G(\overline{r^2}/\overline{r^4})$.**—Since it is not easy to deduce a well-defined range of existence for Ds, the problem has been solved in terms of Dq and G. It is well known[20,21] that an *ab initio* calculation of the mean power radii $\overline{r^n}$ fails to give values in agreement with those obtained experimentally. An assessment of the range of existence of the G ratio has therefore been obtained by relating it to the ratio e'_σ/e'_π (x) for which a range can be deduced intuitively.

Thus from (6) and (8)

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$$G = 6(e'_\sigma + e'_\pi)/14.4(3e'_\sigma - 4e'_\pi) = 6(x + 1)/14.4(3x - 4) \quad (10)$$

A plot of G vs. x is shown in Figure 1; this can be interpreted to infer that with essentially σ-donor ligands (e'_σ large, e'_π small, x large) G approaches 0.14. As the relative π-donor strength increases, G does not vary greatly until x approaches 2, whereupon there is an exponential increase in G. Negative values of G arise if e'_π exceeds 75% of e'_σ, while small positive values of G can arise with π-electron-accepting ligands (e'_π negative, x negative). The relationship between the nature of the ligands and the signs of Dq and G can be summarized as in Table I. The $Dq(-)$ and $G(+)$ combination is impossible since $Dq(-)$ requires e'_π to exceed 75% of e'_σ while this ratio automatically yields a negative value of G (see Figure 1). Consideration of Figure 1 suggests that for most complexes G will lie between −2.0 and +2.0; this range is used for the figures which follow but values of G exceeding 2 have been considered in attempting to fit the experimental data, as described below. A negative value for G is, of course, impossible in a purely crystal-field model, since the radial integrals concerned are inherently positive. By introduction of covalency, G becomes a freely varying semiempirical parameter which can, in principle, be negative and which has lost its significance as a ratio of radial integrals.

TABLE I

Sign of Dq	Sign of G	σ nature of ligand	π nature of ligand
+	+	σ donor (weak or strong)	Weak π donor ($e'_\pi < 75\%\ e'_\sigma$) or π acceptor
+	−	Weak σ donor	Strong π-acceptor ligand ($\lvert e'_\pi \rvert > e'_\sigma$)
−	+	Impossible for real complexes	
−	−	σ donor	Strong π donor ($e'_\pi > 75\%\ e'_\sigma$)

(v) **Ground-State-Energy Space Diagrams.**—It is now possible to deduce which ground states are possible for the various d^n configurations and assuming a chemical significance for the e'_σ and e'_π parameters it is also possible to deduce the chemistry necessary to achieve them. No systematic study of possible ground states for linear molecules (MX_2) together with their probability of occurrence has previously been undertaken. These diagrams, examples of which have been previously published,[10,11] represent the energy base ($E = 0$) of a multidimensional "Tanabe–Sugano" type diagram in which the energies of the various terms are plotted against the various parameters (Dq, Ds, G, B, etc.). Whenever, for particular values of a given variable, an excited state can become the ground state, its potential surface will intersect this $E = 0$ plane; thus such diagrams portray, at a glance, the possible ground states and the values of the parameters necessary to generate them. Note, however, that the lower right quadrant is excluded for all complexes (*vide supra*) and that the upper left quadrant is excluded for halogen derivatives since such ligands are not π acceptors.

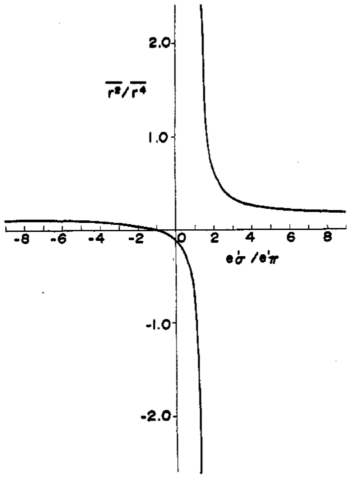

Figure 1.—A plot of the ratio e'_σ/e'_π vs. $\overline{r^2}/\overline{r^4}$ (G). Note that when defined in crystal-field terms, the ratio of the expectation values of $\overline{r^2}$ and $\overline{r^4}$ cannot be negative since both quantities are positive. However, when covalency is taken into account and the ratio considered in a semiempirical fashion, negative values become feasible.

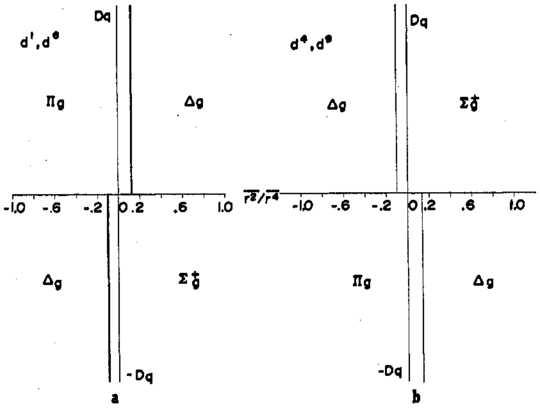

Figure 2.—Ground-state-energy space diagrams for (a) d^1, d^6 ions and (b) d^4, d^9 ions. The boundaries are indicated as thick lines in chemically viable quadrants and weaker lines in chemically nonviable quadrants (see text).

(a) **d^1 and d^6 Species (Figure 2a).**—Most complexes will have both positive Dq and G (*vide supra*) located in the upper right quadrant. The ground state will be Δ_g except for complexes with very low G, *i.e.*, essentially σ-donor complexes with negligible π components to the metal–ligand bond, for which complexes a Π_g ground term may occur. The possibility for both negative Dq and G exists for complexes with primarily π-donor ligands, in the lower left quadrant giving rise to a Σ_g^+ ground state for low negative G and Δ_g for larger negative G values.

(b) **d^4 and d^9 Species (Figure 2b).**—In this case the dominant ground term is Σ_g^+ (upper right quadrant) with the possibility of a Π_g ground term for π-donor ligands (lower left).

(c) **d^2 and d^7 Species (Figure 3a).**—Either a Σ_g^- or Φ_g ground state would seem viable depending upon the relative values of Dq and G (upper right quadrant). If the π-donor nature of the ligand is important, but not predominantly so, a Φ_g ground state is likely. Strong σ donors will generate a Σ_g^- ground state. A Δ_g ground state could arise (lower left) if the π-donor contribution is dominant.

(d) **d^3 and d^8 Species.**—Figure 3b indicates that these species will commonly exist with either Π_g or Δ_g ground states (upper right), with strongly π-donor lig-

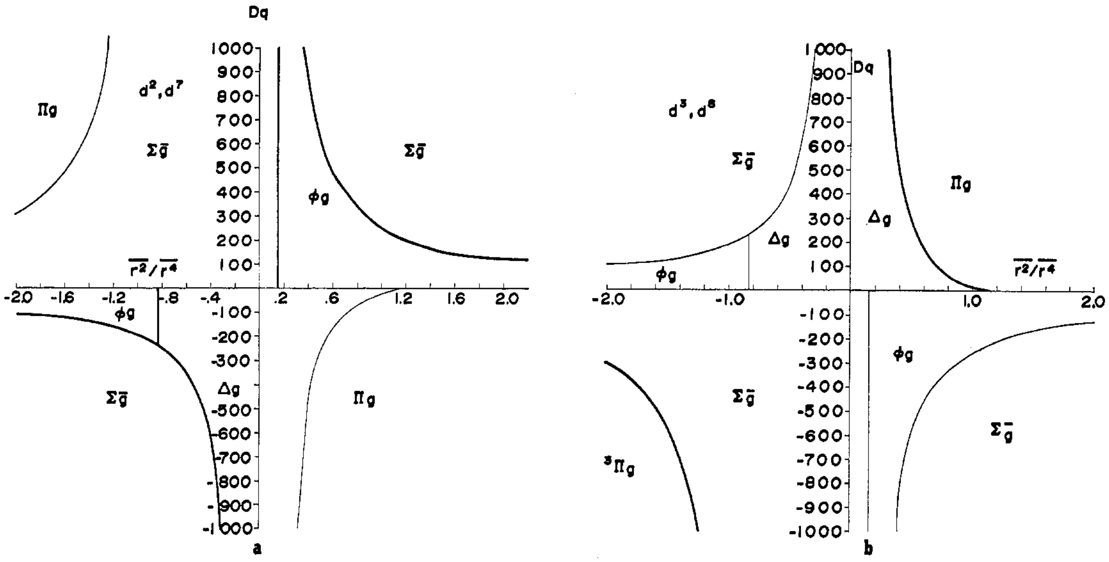

Figure 3.—Ground-state-energy space diagrams for (a) d^2, d^7 ions and (b) d^3, d^8 ions. B = 500 cm^{-1}.

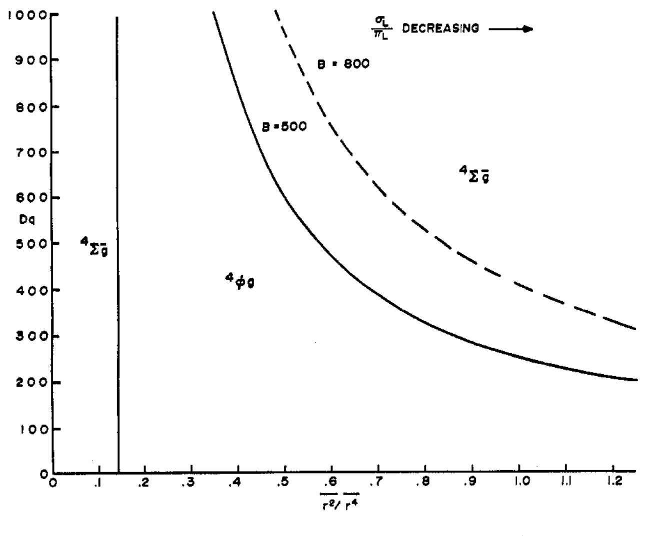

Figure 4.—Ground-state-energy space diagram (upper right quadrant only) for d^7 ions: solid lines, B = 500 cm^{-1}; hatched line, B = 800 cm^{-1}. The boundary at about $\overline{r^2}/\overline{r^4}$ = 1.5 is essentially independent of B.

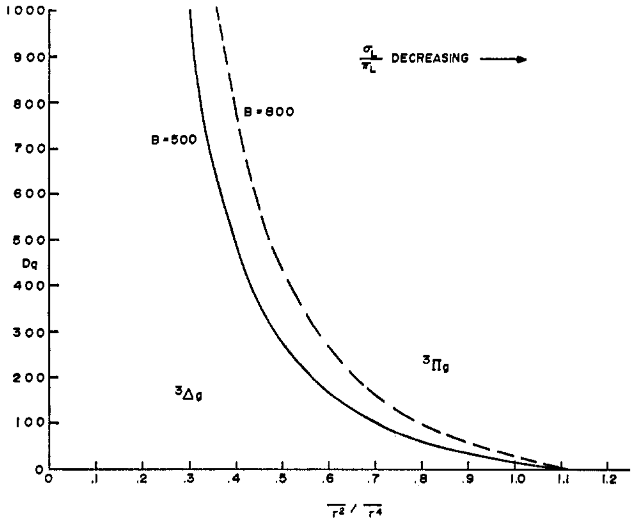

Figure 5.—Ground-state-energy space diagram (upper right quadrant only) for d^8 ions: solid line, B = 500 cm^{-1}; hatched line, B = 800 cm^{-1}. In the region beyond $\overline{r^2}/\overline{r^4}$ = 2.0 with Dq < 100 cm^{-1} the ground state becomes ${}^3\Sigma_g^-$.

ands giving rise to a Σ_g^- ground state (lower left).

Figures 4 and 5 illustrate the upper right quadrant of the diagrams pertinent specifically to cobalt(II) and nickel(II) complexes, respectively, and show the effect of changing the Racah parameter B. The almost vertical boundary in Figure 4 is unaffected by change in B. These diagrams also accentuate that decreasing the ratio of the σ to π character of the metal–ligand bond will move the complexes to larger values of G.

In d^3 and d^8 complexes there exists a region of the Σ_g^- ground term for values of G exceeding 2.0 when matched with very low (<100 cm^{-1}) values of Dq (not illustrated).

(vi) **Assignment of Experimental Data.**—The data will be discussed according to the identity of the central metal ion. Various data sets exist in the literature and there has been extensive speculation as to whether a given data set adequately represents the spectrum of the particular MX_2 species or whether the sample is contaminated with nonlinear impurities. We have chosen those sets of data which have been presented with the most convincing arguments for purity.

(a) **Chromium(II) Dichloride.**—The gas-phase spectrum exhibits[2] two bands at 5400 and 9000 cm^{-1} assignable to spin-allowed transitions. With the two possible ground states Σ_g^+ and Π_g, four assignments are possible (Table II), and all can be fitted to the Hamiltonian yielding the parameters shown in Table II. The first three assignments are eliminated as unreasonable since in i e'_σ is negative, in ii e'_π is greater than e'_σ which is highly improbable, and if iii were correct, the chloride ion would be shown to be a powerful π acceptor, which is also highly improbable. Thus assignment iv is chosen, in agreement with previous authors.[2,9]

(b) **Ferrous Chloride.**—The gas-phase spectrum exhibits[2] bands assignable to spin-allowed transitions at 4600 and 7140 cm^{-1}. From Figure 2b it is evident that the probable ground term is ${}^5\Delta_g$ although ${}^5\Sigma_g^+$

TABLE II

ASSIGNMENTS AND PARAMETERS (CM^{-1}) OF CHROMIUM(II) DICHLORIDE

Assignment	5400 cm^{-1}	9000 (cm^{-1})
i	$^5\Delta_g \leftarrow {}^5\Pi_g$	$^5\Sigma_g{}^+ \leftarrow {}^5\Pi_g$
ii	$^5\Sigma_g{}^+ \leftarrow {}^5\Pi_g$	$^5\Delta_g \leftarrow {}^5\Pi_g$
iii	$^5\Delta_g \leftarrow {}^5\Sigma_g{}^+$	$^5\Pi_g \leftarrow {}^5\Sigma_g{}^+$
iv	$^5\Pi_g \leftarrow {}^5\Sigma_g{}^+$	$^5\Delta_g \leftarrow {}^5\Sigma_g{}^+$

Assignment	Ds	Dq	G	e'_σ	e'_π	Ground state
i	−771.4	−1620	−0.023	−1800	2700	Π_g
ii	−5400	−1260	−0.208	1800	4500	Π_g
iii	−771.4	1530	0.024	2700	−1800	$\Sigma_g{}^+$
iv	−5400	630	0.417	4500	1800	$\Sigma_g{}^+$

would be admissible. Four possible assignments occur but only the two derived from $^5\Delta_g$ will fit the Hamiltonian if Ds is to be negative. The assignments and parameters are given in Table III. Despite the very small value for Dq, assignment i is preferred since it gives reasonable values for e'_σ and e'_π, while assignment ii leads to the chloride ion being a stronger π donor than σ donor to iron, an unlikely event. Choice of assignment i is in agreement with previous authors.[2,9]

TABLE III

ASSIGNMENTS AND PARAMETERS (CM^{-1}) OF FERROUS CHLORIDE

Assignment	4600 cm^{-1}	7140 cm^{-1}
i	$^5\Pi_g \leftarrow {}^5\Delta_g$	$^5\Sigma_g{}^+ \leftarrow {}^5\Delta_g$
ii	$^5\Sigma_g{}^+ \leftarrow {}^5\Delta_g$	$^5\Pi_g \leftarrow {}^5\Delta_g$

Assignment	Ds	Dq	G	e'_σ	e'_π	Ground state
i	−5031	151	1.62	3570	2300	$^5\Delta_g$
ii	−5031	−738	−0.33	2300	3570	$^5\Delta_g$

(c) **Nickel Chloride.**—This species will be considered prior to cobalt chloride since the latter presents special problems. Nickel chloride exhibits two relatively intense peaks at 13,000 and 21,700 cm^{-1} assignable with little doubt to spin-allowed transitions.[1] In addition a very sharp band at 11,700 cm^{-1} and a series of weak multiplet absorptions ascribable to spin-forbidden transitions are observed. A broad plateau beginning below 4000 cm^{-1} and extending until 7000 cm^{-1} may contain several spin-allowed and/or spin-forbidden transitions.

A computer program scanned over a wide range of Dq, B, and G values in the upper right quadrant and searched for *any assignment* which would place spin-allowed bands close to 13,000 and 21,700 cm^{-1} with all other spin-allowed bands either above 21,700 cm^{-1} or in or below the 4000–8000-cm^{-1} region. To minimize the computer time involved, no attempt was made to obtain a fit in the lower left quadrant since, were one to be located, it would be eliminated on the basis that it would infer that the chloride ion was behaving as a stronger π donor than σ donor. Four sets of parameters led to spin-allowed bands in the regions indicated above. All involve a $^3\Pi_g$ ground term. The assignments and parameters are given in Table IV. Assignments i and ii seem untenable on the grounds that (a) it is unlikely that the e'_σ will be more than double the e'_σ values in CrCl_2 and FeCl_2 and (b) the nickel–halogen bond will be very covalent and a B value close to 1000 cm^{-1} seems inconsistent. However neither of these arguments is conclusive in that we do not yet have a feeling for how e'_σ should vary across the transition series and there is some evidence[22] that a strongly π-donating ligand could give rise to a high B value.

TABLE IV

ASSIGNMENTS AND PARAMETERS (CM^{-1}) FOR NICKEL CHLORIDE

Assignment	$^3\Delta_g$	$^3\Sigma_g{}^-$(F)	$^3\Phi_g$	$^3\Pi_g$(P)	$^3\Sigma_g{}^-$(P)
i	4000	4790	13,080	21,685	36,055
ii	4622	4015	12,916	21,760	36,803
iii	2208	1525	6,341	13,051	21,656
iv	2454	879	5,853	12,984	21,701

Assignment	Ds	Dq	G	e'_σ	e'_π	B	Ground state
i	−12,500	858	0.71	9559	5024	979	$^3\Pi_g$
ii	−12,780	706	0.88	9529	5381	999	$^3\Pi_g$
iii	−6,912	320	1.05	5065	3000	700	$^3\Pi_g$
iv	−6,768	200	1.645	4798	3098	725	$^3\Pi_g$

Assignments iii and iv seem more acceptable since the values of e'_σ and e'_π are reconcilable with those for CrCl_2 and FeCl_2 (*vide infra*) and the B values are intuitively reasonable for such a nickel chloride interaction. No distinction can be drawn between iii and iv on the basis of the spin-allowed spectra or the values of the various parameters. However nickel chloride has a very well-defined spin-singlet spectrum with a sharp spike at 11,727 cm^{-1} and regions of weak narrow absorption near 10,000, 11,000, 14,000, 16,000, and 18,000 cm^{-1}. The energy matrices for these transitions,[3] exclusive of spin–orbit coupling, were used as a means of distinguishing the assignments. A program was written which accepted the Dq, G, and B values for assignments i–iv and by varying the value of the Racah C parameter sought any fit which would place a band at 11,727 cm^{-1} and additional transitions near or within the regions indicated above.

Assignment iv yields the best set of data. Using the parameters for this assignment and a value for C of 5436 cm^{-1} (*i.e.*, $C/B = 7.5$) agreement between the calculated and experimental spectra is as shown in Table V. This assignment, at least with regard to the spin-allowed spectrum, agrees with that previously proposed by DeKock and Gruen[2] and by Smith[9] but differs from that of Hougen, *et al.*[1] As can be seen, the overall agreement is very satisfactory; it is important to recognize that this agreement between the calculated spectra and the experimental data (three spin-allowed bands and eight regions of spin-singlet absorption) has been chieved with only four variables (Dq, G, B, and C).

TABLE V

DATA FOR NICKEL CHLORIDE USING ASSIGNMENT iv

	Cm^{-1}			Cm^{-1}	
Transition	Obsd	Calcd	Transition	Obsd	Calcd
$^3\Sigma_g{}^-$(F)		879	$^1\Delta_g$(G)	~16,000	15,466
$^3\Delta_g$(F)		2,454	$^1\Delta_g$(D)	~18,000	18,236
$^3\Phi_g$(F)	4,000–6,000	5,853	$^3\Sigma_g{}^-$(F)	21,700	21,701
$^1\Sigma_g{}^+$(D)	10,000–11,000	10,601	$^1\Pi_g$(G)		26,740
$^1\Pi_g$(D)	11,727	11,727	$^1\Sigma_g{}^+$(G)		27,234
$^3\Pi_g$(P)	13,000	12,984	$^1\Gamma_g$(G)		28,825
$^1\Phi_g$(G)	~14,000	14,717	$^1\Sigma_g{}^+$(S)		55,433

(d) **Variation in the Values of the Orbital Angular Overlap Parameters and the Spectrum of Cobalt**

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[22] B. R. Hollebone, *J. Chem. Soc. A*, 481 (1971).

Chloride.—The variations in e'_σ and e'_π, obtained so far, are consistent with the electron configurations for the various species (Table VI). Thus changes in e'_σ and e'_π may be correlated[23] against the strong-field d-orbital occupation of the ground state indicated above in terms of the δ ($x^2 - y^2$, xy), π (xz, yz), and σ (z^2) antibonding nature of the orbitals concerned. Proceeding from d^4 to d^6 the number of π-antibonding electrons remains constant but a σ-antibonding electron is added. This results in an increase in e'_π since the nuclear charge has increased by 2, but a decrease in e'_σ. From d^6 to d^8 the number of σ-antibonding electrons remains constant but an additional π-antibonding electron is added; thus e'_σ should increase while e'_π might be expected to decrease. In fact both parameters increase. Possibly the increase in nuclear charge offsets the increase in number of π-antibonding electrons. We return to this point below.

TABLE VI

Species	e'_σ, cm^{-1}	e'_π, cm^{-1}
d^4 ($\delta^2\pi^2$) $CrCl_2$	4500	1800
d^6 ($\delta^3\pi^2\sigma$) $FeCl_2$	3570	2300
d^7 ($\delta^4\pi^2\sigma$) $CoCl_2$	?	?
d^8 ($\delta^4\pi^3\sigma$) $NiCl_2$	4798	3098

The problem of band assignment in the spectrum of cobalt chloride has been discussed in depth by Smith.[9] A prominent feature near 14,700 cm^{-1} was assumed by earlier workers[1,2] to be a spin-allowed transition within the d manifold of the linear molecule, while Smith preferred to regard it as an impurity band arising from traces of a tetrahedral species. Weak bands[2] near 10,400 and 18,200 cm^{-1} (or near 20,000 cm^{-1})[1] are also believed[1,2,9] to be due to spin-allowed transitions. A low-temperature (liquid He) matrix spectrum[6] of linear cobalt chloride reveals prominent features near 12,400 and 20,800 cm^{-1} which are probably spin-allowed bands and which likely correspond to the weak bands alluded to above in the gas-phase spectrum. Alternatively the 12,400-cm^{-1} band may correspond with prominent shoulders near 12,000 cm^{-1} in the gas-phase spectrum. Unfortunately the matrix spectrum excluded the 14,000-cm^{-1} region. The uncertainty makes it impossible to assign the experimental data with any degree of conviction. It is more logical to determine whether a suitable choice of $e'_{\sigma,\pi}$ parameters could lead to a predicted spectrum compatible with the existing spectroscopic data. Linear extrapolation of the e'_σ parameters for d^6 and d^8 to d^7 suggests e'_σ($CoCl_2$) $\simeq$ 4200 cm^{-1}. Extrapolation of e'_π from d^4 and d^6 to d^7 suggests e'_π($CoCl_2$) $\simeq$ 2550 cm^{-1}. Inclusion of the d^8 datum for e'_π suggests that this value for d^7 may be as high as 2700 cm^{-1}. A program varied B and the e'_σ and e'_π parameters (near the above values) to search for fits to the aforementioned features in the cobalt chloride spectrum, with the results shown in Table VII. Both assignments are consistent with the general features of the spectrum of cobalt chloride, suggesting that the general approach is valid. The ground state ($^4\Sigma_g^-$) differs from that assumed by earlier workers who preferred $^4\Phi_g$. However, it is clear that these compounds do not lie far from the ground-state crossover. The transitions to the components of the P term are formally "two-electron" transitions which may account for the weakness of the band assigned to $^4\Sigma_g^-$(P). The somewhat greater intensity of the $^4\Pi_g$(P) component, at least as seen in the matrix spectrum, may arise through "intenisty stealing" from charge-transfer bands lying at higher energies.

TABLE VII

PARAMETERS (CM^{-1}) OF COBALT CHLORIDE

Assignment	Ds	Dq	G	e'_σ	e'_π	B
i	−5948	297	0.97	4390	2550	583
ii	−5704	211	1.31	4165	2550	667

Assignment	$^4\Pi_g$	$^4\Delta_g$	$^4\Phi_g$	$^4\Sigma_g^-$(P)	$^4\Pi_g$(P)
i	4394	20,792	1856	12,456	24,470
ii	2804	14,197	210	10,425	21,270

(e) **Copper Chloride and Vanadium Chloride.**—For these species there are insufficient experimental data to solve unequivocally for the parameter values. Copper chloride exhibits two bands, at 9000 and 18,000 cm^{-1}. The intensity of the latter band suggests that it is charge transfer in origin[2] but it has not always been so assigned.[1] Smith[9] concluded that Hougen[1] was in fact correct in assigning the 9000-cm^{-1} band to the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ transition and placed the $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ transition in the 19,000-cm^{-1} region where it is obscured by the charge-transfer band. Smith argued that if the alternate assignment[2] pertains, *i.e.*, the 9000-cm^{-1} band is assigned as $^2\Delta_g \leftarrow {}^2\Sigma_g^+$, then the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ transition should lie near 5000 cm^{-1} where it should have been observed. We suggest nevertheless that this latter assignment[2] is indeed correct. If the e'_σ and e'_π parameters used above to explain the d^4, d^6, d^7, and d^8 species are extrapolated linearly to d^9, then $e'_\sigma \simeq$ 5400 cm^{-1} and $e'_\pi \simeq$ 3300 cm^{-1}. These lead to the following transition energies: $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ at 4200 cm^{-1} (ν_1) and $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ at 10,800 cm^{-1} (ν_2). While agreement is not perfect, it seems unlikely that the $e'_{\sigma,\pi}$ values have been so misjudged as to place the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ transition at 9000 cm^{-1}. Note that a small increase in e'_π of, say, 100 cm^{-1} has little effect on ν_2 but moves ν_1 below 3000 cm^{-1} outside the range of the instrumentation used to date.

The spectrum of gaseous vanadium chloride exhibits a broad structured band near 14,500 cm^{-1} with lower energy peaks at 9600 and 10,700 cm^{-1}. These have been assigned as transitions to the components of the P term.[2] In view of the additional parameter B and the fact that a meaningful extrapolated value of e'_σ cannot be obtained (the V(II) species has no σ-antibonding electrons and there is only one example, d^4, of such a species to extrapolate from) no significant comments can be made about this assignment, as far as the above treatment is concerned.

(f) **Nature of the Metal–Halogen Bond.**—Application of the orbital angular overlap model in a semiempirical fashion leads to a consistent picture of the electronic spectra of linear transition metal dihalides. The e'_σ values closely parallel the occupation numbers of the σ-antibonding level consistent with a covalent metal–halogen interaction. The magnitude of the e'_π parameters suggests a very considerable π-donor contribution to the bond consistent with the belief that the bond lengths in these complexes, by virtue of

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[23] The discussion should preferably be based on the e_σ and e_π parameters which are related[18] to the primed parameters *via* $e'_\sigma = e_\sigma - e_\delta$ and $e'_\pi = e_\pi - e_\delta$. However the e_δ parameter is likely to be very small.

the low coordination number, will be considerably shorter than in tetrahedral or octahedral derivatives of these ions. The fact that the e'_π parameters increase monotonically across the transition series and do not follow the occupation numbers of the π orbitals suggests a considerable electrostatic polarization interaction similar to that proposed[19] to occur in fluorochromium(III) derivatives.

Smith[9] formally separated the covalent from the electrostatic interaction in these complexes by defining the energies E_1 and E_2 as functions of the orbital angular overlap parameters and of the crystal-field radial integrals a_n. In dealing with the experimental data, values of E_1 and E_2 are derived and broken down into covalent and electrostatic components by direct calculation of the overlap and radial integrals. As a consequence of this calculation there is a monotonic increase in σ^* from Cr(II) to Cu(II), which does not therefore follow the σ occupation numbers, as far as Cr(II) and Fe(II) are concerned, while with the exception of Cu(II), π^* is almost independent of the metal ion, an observation which seems difficult to justify. While the fault may lie not so much with the approach but rather with the procedures by which the various parameters were calculated, it would seem more profitable at this time to combine the electrostatic and covalent parameters together within e'_σ and e'_π as inferred in our treatment.

Because of the large amount of spectroscopic data needed to define, unequivocally, values of the $e'_{\sigma,\pi}$ parameters, there is little information in the literature with which to compare the values derived here. In the complex $Ni(NH_3)_4(NCS)_2$ the parameter $e'_\sigma(N)$ is 3500–4000 cm^{-1} while the e'_π parameter is very small.[17] In a wide series of six-coordinate tetragonal nickel complexes,[17,24] $d\pi$ (being $e'_\pi(Z) - e'_\pi(L)$ in NiL_4Z_2) is always very small suggesting that the e'_π values in these complexes are very small. Certainly it was concluded[17] that π bonding plays very little part in six-coordinate nickel(II) derivatives, unlike the situation observed with the analogous chromium(III) derivatives.[19] The value of close to 5000 cm^{-1} for $e'_\sigma(Cl)$ in gaseous nickel chloride is consistent with the value for $e'_\sigma(N)$ for $Ni(NH_3)_4(NCS)_2$ to the extent that changing coordination number from 6 to 2 might generally be expected to increase e'_σ by virtue of decreasing the internuclear nickel–ligand distance. Note that if $e'_\pi(Cl)$ in octahedral complexes is presumed to be zero, then from the observation that $10Dq = 7200$ cm^{-1} for a hexacoordinate chloronickel(II) complex,[20] $e'_\sigma(Cl) = 2400$ cm^{-1} in octahedral complexes. A doubling of this value in linear gaseous $NiCl_2$ does not seem unreasonable.

The success of this treatment in solving a considerable amount of data in terms of a small number of variables suggests that the orbital angular overlap paramenters do have chemical significance. It seems that they can be used, in a relative sense, as a measure of σ and π bonding. Accepting this, then clearly the π interaction in these gaseous dihalides is extremely important. Since, as alluded to above, these parameters contain an electrostatic component when derived in a semiempirical fashion, the π interaction may not be entirely covalent in orgin. A strong electrostatic component may be present in view of the observation that the e'_π parameters do not follow the π occupation numbers. In closing it is of interest to note that as a consequence of this strong π interaction, the $10Dq$ values vary a great deal across the transition series and are of little value in themselves to identify the nature of the metal–ligand bond. In complexes of higher coordination number where e'_π is much smaller, the Dq values mimic changes in e'_σ and are therefore of greater qualitative significance.

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(24) M. Keeton and A. B. P. Lever, unpublished observations.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
CANOGA PARK, CALIFORNIA 91304

Chlorine Trifluoride Oxide. I. Preparation and Properties

BY D. PILIPOVICH,* C. B. LINDAHL, C. J. SCHACK, R. D. WILSON, AND K. O. CHRISTE

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Chlorine trifluoride oxide, ClF_3O, has been prepared by either direct fluorination of Cl_2O, $NaClO_2$, or $ClONO_2$, or by glow discharge of F_2 in the presence of solid Cl_2O. A number of physical properties are reported as well as the ^{19}F nmr spectrum and the mass cracking pattern.

Introduction

Chlorine trifluoride oxide, ClF_3O, was prepared and characterized at Rocketdyne in 1965.[1] However, these results were not reported in the open literature. Recently, Bougon, Isabey, and Plurien have independently discovered[2] ClF_3O. In this paper, we report several synthetic routes and some physical and spectroscopic properties for ClF_3O.

Experimental Section

Materials and Apparatus.—Chlorine nitrate, $ClONO_2$, was prepared by the method of Schack.[3] Dichlorine oxide, Cl_2O, was generated as required from a Cl_2–HgO mixture as reported[4] by Schack and Lindahl. Mercuric oxide was prepared by the method of Cady.[5] Sodium chlorite was purchased from Matheson Coleman and Bell. Alkali metal fluorides were obtained from American Potash and Chemical Co. Prior to their use, they

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