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Ligand Field Splittings in Non-Cubic Complexes. V.* Analysis of the d-d Spectra of the Gaseous Dichlorides of the First Transition Series

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The d–d spectra of gaseous VCl_2, $CrCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, and $CuCl_2$ are discussed in terms of ligand field theory. The Tanabe-Sugano matrices for linear ($D_{\infty h}$) d^3, d^7, and d^8 systems are given and the d-orbital splitting parameters are determined for each molecule. The results can be satisfactorily rationalized by empirical MO calculations, based on the angular overlap model. Alternative assignments of the spectra of VCl_2, $CoCl_2$, and $CuCl_2$ are discussed in detail.

Introduction

The application of ligand field theory to the optical and magnetic properties of transition metal ions in crystalline solids and in solution is now familiar to most inorganic chemists. However, the study of small gaseous molecules containing metals with a partly-filled shell can be much more rewarding in many ways. The electronic absorption bands are often very sharp, revealing much vibronic structure, and it may not be long before *ab initio* SCF calculations are performed on molecules like VCl_2.

A number of workers[1-6] have measured the electronic spectra of the molecular dichlorides of the first transition series, with the exceptions of $MnCl_2$, where the spin-forbidden d–d bands are very weak, and $TiCl_2$, wich is unstable with respect to disproportionation to Ti metal and higher chlorides.[7] Hougen, Leroi, and James[1] reported the spectra of $CuCl_2$, $NiCl_2$, and $CoCl_2$, and presented interpretations on the basis of crystal field arguments. Their analysis was based on a weak-field scheme in $D_{\infty h}$ symmetry, and free–ion values of the term separations ^3P–^3F and ^4P–^4F in Co^{2+} and Ni^{2+} were assumed. The bands observed at 9 kK and 18 kK in $CuCl_2$ were assigned to the d–d transitions $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ and $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ respectively, and the crystal field parameters required to fit these energies were used in their discussion of the spectra of $CoCl_2$ and $NiCl_2$.

Subsequently, Jørgensen[8] questioned the assignment of the 18 kK band in $CuCl_2$ to a d–d transition, on the grounds that the high molar extinction coefficient reported by Hougen *et al.* ($\varepsilon = 500$) was more consistent with a charge transfer band, rather than a Laporte-forbidden d–d band. DeKock and Gruen supported this proposal by making careful intensity measurements, and quoted a molar extinction coefficient of over 3000 ℓ mole^{-1} cm^{-1} for the higher energy band in $CuCl_2$, which they observed at 19.0 kK. The 9.0 kK band was then assigned to the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition, while the $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition was believed to lie at an energy lower than 4 kK, outwith the region of the spectrum accessible to DeKock and Gruen. New crystal field parameters were chosen, and the d–d spectra of VCl_2, $NiCl_2$, and $CoCl_2$ were reinterpreted using these parameters in a weak-field scheme with the assumption of a modest (14%) nephelauxetic reduction in the free-ion separations ^3P–^3F and ^4P–^4F.

In the present series of papers,[9-11] we have shown how the d-orbital splittings in copper(II) compounds can be satisfactorily rationalised in terms of an empirical MO approach, based on the angular overlap model and including crystal field effects. We have successfully fitted the d–d spectra of square-coplanar, tetragonal octahedral, trigonal bipyramidal and distorted tetrahedral chlorocuprates(II) to a single freely-chosen parameter, the ratio $\sigma^*/(S^\sigma_{mx})^2$. The use of the same value of this parameter in a calculation of the d-orbital splitting in $CuCl_2$[12] placed the $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition at about 10 kK, with the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition several kK higher in energy, in agreement with the original assignment of Hougen *et al.*[1] In this paper we extend the treatment to the other gaseous dichlorides of the first transition series, with a view to obtaining reliable values of the ligand field splitting parameters and examining how far they can be rationalised in terms of the angular overlap theory. For completeness, we include the previously published results for $CuCl_2$, with some additional discussion.

Outline of Theory

Throughout this paper we assume, following pre-

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(2) G. E. Leroi, T. C. James, J. T. Hougen, and W. Klemperer, *J. Chem. Phys.* 36, 2879 (1962).

(3) D. E. Mulligan, M. E. Jacox, and J. D. McKinlay, *J. Chem. Phys.* 42, 902 (1965).

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(5) C W. De Kock and D. M. Gruen, *J. Chem. Phys.* 44, 4387 (1966).

(6) J. R. Clifton and D. M. Gruen, *Appl. Spectry.* 29, 53 (1970).

(7) M. Farber and A. J. Darnell, *J. Chem. Phys.* 25, 526 (1956).

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

(9) D. W. Smith, *J. Chem. Soc.* (A), 1708 (1969).

vious workers, that the gaseous dichlorides of the first transition series are linear ($D_{\infty h}$). Since no unequivocal structure determinations have been performed, this assumption is worthy of some discussion. Gaseous $ZnCl_2$ has been studied by electron diffraction[13] and was found to be linear, with a Zn—Cl distance of 2.05 Å. Molecular beam studies[14] have shown that some alkaline earth dihalides are bent, but it appears that the propensity for C_{2v} symmetry decreases in the series $MF_2 > MCl_2 > MBr_2 > MI_2$. Since NiF_2 was found to be linear, it seems reasonable to suppose that the dichlorides of the first transition series are also linear. The infra-red spectra of $CuCl_2$, $NiCl_2$, and $CoCl_2$ in the gas phase[1,15] and of $NiCl_2$ in an argon matrix[3] are consistent with $D_{\infty h}$ symmetry, although the gas phase spectra are complicated by the presence of the dimeric species M_2Cl_4. While electron diffraction data would clearly be desirable in order to confirm the linear configuration, it seems reasonably safe to assume $D_{\infty h}$ symmetry. The lack of data on M—Cl bond lengths is unfortunate, however.

In a linear molecule, the d-orbitals are split into three levels: $\sigma_g^+(d_{z^2})$, $\pi_g(d_{xz,yz})$ and $\delta_g(d_{xy,x^2-y^2})$. Henceforth we shall omit all subscripts and superscripts in writing the symmetry labels. Qualitative crystal field arguments suggest the relative one-electron energies to $\sigma > \pi > \delta$. MO theory leads to the same ordering; the σ-orbital is σ-antibonding, the δ orbitals nonbonding and the π orbitals π-antibonding. The angular overlap model[16-20] enables us to set these arguments on a more quantitative basis. The extent to which a d-orbital is destabilized by covalent bonding is assumed to be proportional to the square of the group overlap integral G_{mx} between the d-orbital and the appropriate symmetry-adapted ligand group orbital. This result is obtained from second-order perturbation theory and depends on the Wolfsberg-Helmholz approximation[21] for the off-diagonal matrix elements H_{mx}. The validity of this approximation has been questioned[22] and other semi-empirical prescriptions for H_{mx} have been offered, notably that of Cusachs,[23] but for simplicity we shall abide by the formulation in terms of the Wolfsberg-Helmholz approximation.

The angular overlap treatment leads to the following expressions for the one-electron energies in terms of the covalence parameters σ* and π* for a linear MCl_2 molecule:

$$E(\sigma) = 10\sigma^*$$

$$E(\pi) = 10\pi^*$$

$$E(\delta) = 0$$

If we now apply the perturbation of point charges located at the ligand atoms, the energies become:

$$E(\sigma) = 10\sigma^* + 2a_0 + (4/7)a_2 + (4/7)a_4$$

$$E(\pi) = 10\pi^* + 2a_0 + (2/7)a_2 - (8/21)a_4$$

$$E(\delta) = 2a_0 - (4/7)a_2 + (2/21)a_4$$

$a_n = q\langle r^n \rangle / R^{n+1}$, where $\langle r^n \rangle = \int_0^\infty R_{3d}^2 r^{n+2} dr$ and R is the metal-ligand distance.

The ligand field splitting is described by two parameters E_1 and E_2, given by:

$$E_1 = E(\pi) - E(\delta) = 10\pi^* + (6/7)a_2 - (10/21)a_4 \quad (1)$$

$$E_2 = E(\sigma) - E(\delta) = 10\sigma^* + (8/7)a_2 + (10/21)a_4 \quad (2)$$

Before attempting to calculate E_1 and E_2 from these expression, we shall analyse the experimental data in order to extract values of the splitting parameters which are consistent with the spectra.

Analysis of Experimental Data

(a) *$CuCl_2$*. In this relatively simple d^9 (one-positron) system, assuming that the relative energies of the d-orbitals are as proposed in the previous section, the ground state will be $^2\Sigma$, arising from the configuration $\delta^4 \pi^4 \sigma$. The d—d excited states are $^2\Pi$, arising from the configuration $\delta^4 \pi^3 \sigma^2$, and $^2\Delta$, arising from the configuration $\delta^3 \pi^4 \sigma^2$. The transition energies will be simply:

$$E(^2\Sigma \rightarrow {}^2\Pi) = E_2 - E_1$$

$$E(^2\Sigma \rightarrow {}^2\Delta) = E_2$$

This assumes that the two-electron interactions between core electrons and valence electrons are the same in the ground state and the excited states. An appreciable degree of symmetry-restricted covalence[24] will invalidate this assumption. We have discussed this point previously,[9] and the errors incurred are inherent in all simple discussions of d^1 and d^9 spectra. The success of the angular overlap model in dealing with such systems suggests that such errors are of little importance, or there are fortuitous cancellations.

As we have mentioned earlier, the electronic spectrum of gaseous $CuCl_2$ shows bands at 9.0 and 19.0 kK. If we reject the assignment of the latter band to a d—d transition, two possibilities arise:

(i) The 9 kK is the $^2\Sigma \rightarrow {}^2\Pi$ transition, with the $^2\Sigma \rightarrow {}^2\Delta$ transition at higher energy, obscured by the intense band at 19 kK.

(ii) The 9 kK is the $^2\Sigma \rightarrow {}^2\Delta$ transition, and the $^2\Sigma \rightarrow {}^2\Pi$ transition lies below 4 kK, outwith the range covered experimentally. Thus, *either* E_2 must be 15-18 kK and $E_1 = 6$-9 kK, *or* $E_2 = 9$ kK and $E_1 < 5$ kK. We shall be in a position to decide between these alternatives after a detailed examination of the spectra of the other dichlorides.

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(b) *$NiCl_2$*. In this d^8 (two-positron) system, singlet and triplet states can arise. We consider only the latter, since the ground state is most likely to be $^3\Pi$, arising from the configuration $\delta^4\ \pi^3\ \sigma$, and the most intense bands will be triplet-triplet transitions. The strong-field configurations and the triplet states arising from these have been given previously[25] and are:

$$\delta^4\pi^3\sigma : {}^3\Pi$$
$$\delta^3\pi^4\sigma : {}^3\Delta$$
$$\delta^4\pi^2\sigma^2 : {}^3\Sigma$$
$$\delta^2\pi^4\sigma^2 : {}^3\Sigma$$
$$\delta^3\pi^3\sigma^2 : {}^3\Phi, {}^3\Pi$$

The weak field matrices have been given previously;[1,5,25] in this work we adopt the strong field approach.[26] The two-positron basis functions are as follows:

$$(\pi_a\sigma) = {}^3\Pi_a(\pi\sigma)$$
$$(\pi_b\sigma) = {}^3\Pi_b(\pi\sigma)$$
$$(\delta_a\sigma) = {}^3\Delta_a(\delta\sigma)$$
$$(\delta_b\sigma) = {}^3\Delta_b(\delta\sigma)$$
$$(\pi_a\pi_b) = {}^3\Sigma(\pi^2)$$
$$(\delta_a\delta_b) = {}^3\Sigma(\delta^2)$$
$$2^{-1/2}[(\delta_a\pi_a)-(\delta_b\pi_b)] = {}^3\Pi_b(\delta\pi)$$
$$2^{-1/2}[(\delta_a\pi_a)+(\delta_b\pi_b)] = {}^3\Pi_a(\delta\pi)$$
$$2^{-1/2}[(\delta_a\pi_a)+(\delta_b\pi_b)] = {}^3\Phi_b(\delta\pi)$$
$$2^{-1/2}[(\delta_a\pi_a)-(\delta_b\pi_b)] = {}^3\Phi_a(\delta\pi)$$

In these expressions, π_a and π_b refer to the d_{xz} and d_{yz} orbitals respectively, while δ_a and δ_b refer to the d_{xy} and $d_{x^2-y^2}$ orbitals respectively. We can now set out the Tanabe-Sugano matrices. In the expressions which follow, the diagonal elements are referred to the lowest orbital energy of the system, corresponding to the configuration $\delta^4\ \pi^4$. The Racah parameter A is left out. We find:

$${}^3\Phi(\delta\pi) : 2E_2-E_1-8B$$
$${}^3\Delta(\delta\sigma) : E_2-8B$$

$^3\Pi$	$\delta\pi$	$\pi\sigma$
$\delta\pi$	$2E_2-E_1-2B$	$3\sqrt{6}B$
$\pi\sigma$	$3\sqrt{6}B$	E_2-E_1+B

$^3\Sigma$	δ^2	π^2
δ^2	$2E_2+4B$	$-6B$
π^2	$-6B$	$2(E_2-E_1)-5B$

As a check, we may note that in the limit of an infinitely weak field, where E_1 and $E_2 \rightarrow O$, we obtain two states of energies 7B and −8B, corresponding to the free ion terms ^3P and ^3F respectively, separated by 15B.

This analysis ignores spin-orbit coupling completely. This can be quite a serious matter; the high spin-orbit coupling constant of Ni^{2+} ($\zeta_{3d}=630\ cm^{-1}$) can lead to appreciable splittings of the π, Δ, and Φ states, and mix triplets with singlets. The weak field matrices including spin-orbit coupling have been given by DeKock and Gruen.[27] We shall not include such effects explicitly, but they must be borne in mind.

Expansion of the $^3\Pi$ and $^3\Sigma$ determinants and the assumption of a $^3\Pi$ ($\pi\sigma$) ground state lead to the following expressions for the d—d transitions in $NiCl_2$:

$${}^3\Pi(\pi\sigma)\rightarrow{}^3\Delta(\delta\sigma) = -\tfrac{1}{2}E_2+E_1-7.5B+\tfrac{1}{2}(E_2^2-6E_2B-8E_1B+225B^2)^{1/2}$$

$${}^3\Pi(\pi\sigma)\rightarrow{}^3\Sigma(\pi^2) = \tfrac{1}{2}E_2+\tfrac{1}{2}(E_2^2-6E_2B-8E_1B+225B^2)^{1/2} -\tfrac{1}{2}(4E_1^2+28E_1B+225B^2)^{1/2}$$

$${}^3\Pi(\pi\sigma)\rightarrow{}^3\Phi(\delta\pi) = \tfrac{1}{2}E_2-7.5B+\tfrac{1}{2}(E_2^2-6E_2B-8E_1B+225B^2)^{1/2}$$

$${}^3\Pi(\pi\sigma)\rightarrow{}^3\Pi(\delta\pi) = (E_2^2-6E_2B-8E_1B+225B^2)^{1/2}$$

$${}^3\Pi(\pi\sigma)\rightarrow{}^3\Sigma(\delta^2) = \tfrac{1}{2}E_2+\tfrac{1}{2}(4E_1^2+28E_1B+225B^2)^{1/2} +\tfrac{1}{2}(E_2^2-6E_2B-8E_1B+225B^2)^{1/2}$$

The spectrum measured by DeKock and Gruen[5] shows the following principal features:

(i) A weak, broad, highly-structured absorption in the region 4-8 kK, with shoulders at 7.3 kK and 6.2 kK, a peak at 5.4 kK and a plateau extending to the limit of detection at 4 kK.

(ii) Weak absorption around 10 kK and a sharp peak at 11.7 kK, probably due to singlet excited states.

(iii) A relatively intense, structured absorption centred on about 13.0 kK.

(iv) At higher energy, a series of weak bands and shoulders, probably due to singlet states, followed by an intense peak at 21.1 kK.

Two assignments appear to be feasible:

(A) That of Hougen *et al.*[1] They assigned the near infra-red absorption around 5 kK to $^3\Pi\rightarrow{}^3\Sigma$ (π^2), $^3\Delta$, the 13 kK band to $^3\Pi\rightarrow{}^3\Phi$ and the 21 kK to $^3\Pi\rightarrow{}^3\Pi$, with the $^3\Pi\rightarrow{}^3\Sigma$ (δ^2) transition at higher energy and masked by the intense charge transfer absorption which begings to set in beyond 25 kK. This assignment was based on the crystal field splittings obtained by their analysis of the spectrum of $CuCl_2$, with $E_1=9.0$ kK and $E_2=18.0$ kK. However, in their weak field treatment they did not allow for any nephelauxetic reduction of the free ion term separation ^3P—^3F.

(B) The assignment of DeKock and Gruen.[5,27] They asigned the infra-red absorption to $^3\Pi\rightarrow{}^3\Phi$, the 13 kK band to $^3\Pi\rightarrow{}^3\Pi$ and the 21 kK band to $^3\Pi\rightarrow{}^3\Sigma$ (δ^2). This assignment was based on the splitting parameters found with some certainty for $FeCl_2$ and $CrCl_2$. A 14% reduction of the free-ion value of ^3P—^3F was assumed, in a weak-field treatment.

We shall try to decide between these assignments by calculating values of E_1 and E_2 which best fit the experimental data. Let us first assume that Assignment A is correct. We could, in principle, equate the expressions given above to the three transition energies and solve for the unknowns E_1, E_2, and B. Unfortunately, the near infrared band around 6 kK is

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not too well defined. We therefore set the expressions for the transition energies $^3\Pi \rightarrow ^3\Phi$ and $^3\Pi \rightarrow ^3\Pi$ equal to 13.0 kK and 21.1 kK respectively, and solve for E_1 and E_2 over a range of reasonable values for B. We must now consider what values of B are to be regarded as reasonable. DeKock and Gruen[5,27] proposed a 14% reduction of the free-ion term separation ^3P–^3F on the basis that this value had previously been successfully used[28] in the interpretation of the spectrum of $CoCl_4^{2-}$. However, subsequent work[29] on $NiCl_4^{2-}$ indicated a much larger nephelauxetic effect, with B taken as 0.75 kK, 0.72 of the free-ion value. The nephelauxetic effect seems to be much the same in $NiCl_4^{2-}$ as in solid $NiCl_2$, for which a value of B of 0.76 kK has been quoted.[30] We might therefore be justified in using a similar value of B in gaseous $NiCl_2$ on the grounds that B does not seem to be sensitive to stereochemistry and coordination number. This is consistent with the angular overlap model, which assumes that the fractional charge on the metal is not very dependent on the geometry, so that the central-field contribution to the nephelauxetic effect is effectively constant. Provided that the reduction in B from the free-ion value due to symmetry-restricted covalence[24] is not very different in gaseous $NiCl_2$, it seems reasonable to use the same value of B as in $NiCl_4^{2-}$. However, in view of the doubts which might be cast on this, we shall calculate E_1 and E_2 for three values of B, 0.80 kK, 0.75 kK, and 0.70 kK. We feel that B probably falls within this range and is most unlikely to lie much beyond it. The expressions for the transition energies $^3\Pi \rightarrow ^3\Phi$ and $^3\Pi \rightarrow ^3\Pi$ are then readily solved to give E_1 and E_2. The results are shown in Table I, along with calculated values of the transition energies $^3\Pi \rightarrow ^3\Delta$ and $^3\Pi \rightarrow ^3\Sigma$ (π^2). The values of E_1 and E_2 look distinctly unlikely, and the ground state is predicted to be $^3\Delta$. Even with the assumption of a $^3\Delta$ ground state, it is not possible to obtain reasonable values of E_1 and E_2 while allowing for the nephelauxetic effect. We are therefore forced to reject Assignment A.

Table I. Splitting parameters and predicted transition energies for $NiCl_2$ on the basis of Assignment A. All energies are in kK.

B	0.70	0.75	0.80
E_1	15.4	16.2	16.9
E_2	−28.8	−21.7	−15.0
$^3\Pi \rightarrow ^3\Delta$	−31.2	−24.8	−18.9
$^3\Pi \rightarrow ^3\Sigma(\pi^2)$	−10.0	− 0.4	6.1

We now turn to the possibility that Assignment B is the correct one. The expressions given above for the transition energies $^3\Pi \rightarrow ^3\Pi$ and $^3\Pi \rightarrow ^3\Sigma$ (δ^2) are equated to 13.0 kK and 21.1 kK respectively. Assuming that only positive solutions are acceptable the equations are easily solved by graphical means. The results are given in Table II. The values found for E_1 and E_2 are seen to be quite reasonable over the range of B-values considered. Moreover, the calculated transition energies for $^3\Pi \rightarrow ^3\Phi$ and $^3\Pi \rightarrow ^3\Sigma$ (π^2) are consistent with the broad infra-red absorption in the region 4-8 kK. Thus we prefer Assignment B, in agreement with DeKock and Gruen[5,27] but for different reasons: they preferred Assignment B to Assignment A on the basis of a different assignment of the spectrum of $CuCl_2$ to that on which Assignment A was based. Our values of the splitting parameters E_1 and E_2 are also rather larger than those proposed by DeKock and Gruen since we assume a larger nephelauxetic effect.

Table II. Splitting parameters and predicted transition energies for $NiCl_2$ on the basis of Assignment B. All energies are in kK.

B	0.70	0.75	0.80
E_1	5.8	5.4	5.2
E_2	11.8	11.0	10.4
$^3\Sigma \rightarrow ^3\Delta$	7.1	6.6	6.3
$^3\Sigma \rightarrow ^3\Sigma(\pi^2)$	3.7	2.9	2.3

The inclusion of spin-orbit coupling would probably have a significant effect on our values of the splitting parameters, perhaps a few hundred wavenumbers. A more serious source of error is likely to arise from our assumption of only a single value of B. Allowance for the effects of symmetry-restricted covalence would require the use of five different values of B, corresponding to two-positron interactions of the types ($\sigma\delta$), ($\pi\pi$), ($\delta\delta$), ($\sigma\pi$), and ($\delta\pi$). All these factors must be taken into account in assessing the validity of the splitting parameters given in Table II.

(c) *$CoCl_2$*. The d^7 (three-positron) configuration gives rise to quartet states and doublet states. If the ground state is assumed to be $^4\Phi$, arising from the configuration $\delta^3\ \pi^3\ \sigma$, the most prominent features of the spectrum will be transitions to quartet states. Again, we neglect spin-orbit coupling. The strong-field configurations and the quartet states arising from them are:

$\delta^3\pi^3\sigma : {}^4\Phi, {}^4\Pi$
$\delta^3\pi^2\sigma^2 : {}^4\Delta$
$\delta^2\pi^3\sigma^2 : {}^4\Pi$
$\delta^4\pi^2\sigma : {}^4\Sigma$
$\delta^2\pi^4\sigma : {}^4\Sigma$

The three-positron basis functions are found to be:

$$(\delta_a\delta_b) = {}^4\Sigma(\delta^2\sigma)$$

$$(\pi_a\pi_b\sigma) = {}^4\Sigma(\pi^2\sigma)$$

$$(\delta_a\delta_b\pi_a) = {}^4\Pi_a(\delta^2\pi)$$
$$(\delta_a\delta_b\pi_b) = {}^4\Pi_b(\delta^2\pi)$$

$$(\delta_a\pi_a\pi_b) = {}^4\Delta_a$$
$$(\delta_b\pi_a\pi_b) = {}^4\Delta_b$$

$$2^{-1/2}[(\delta_a\pi_a\sigma) + (\delta_b\pi_b\sigma)] = {}^4\Phi_b$$
$$2^{-1/2}[(\delta_a\pi_b\sigma) - (\delta_b\pi_a\sigma)] = {}^4\Phi_a$$

$$2^{-1/2}[(\delta_a\pi_a\sigma) - (\delta_b\pi_b\sigma)] = {}^4\Pi_b(\delta\pi\sigma)$$
$$2^{-1/2}[(\delta_a\pi_b\sigma) + (\delta_b\pi_a\sigma)] = {}^4\Pi_a(\delta\pi\sigma)$$

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(29) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc. 83*, 4164 (1961).
(30) O. Bostrup and C K. Jørgensen, *Acta Chem. Scand. 11*, 1223 (1957).

The Tanabe-Sugano matrices are set out below. The diagonal elements are relative to the lowest orbital configuration $\delta^4\ \pi^3$ and the terms involving the Racah parameter A are omitted.

$$^4\Phi : E_2—15B$$

$$^4\Delta : 2E_2—E_1—15B$$

$^4\Pi$	$\delta^2\pi$	$\delta\pi\sigma$
$\delta^2\pi$	$2E_2—6B$	$3\sqrt{6}B$
$\delta\pi\sigma$	$3\sqrt{6}B$	$E_2—9B$

$^4\Sigma$	$\pi^2\sigma$	$\delta^2\sigma$
$\pi^2\sigma$	$E_2—E_1—3B$	$6B$
$\delta^2\sigma$	$6B$	$E_1+E_2—12B$

As a check, we note that in the limit of a negligible ligand field (E_1, $E_2 \rightarrow 0$) the states converge to the energies of the ^4F and ^4P free-ion terms, separated (as in Ni^{2+}) by 15B.

Expansion of the $^4\Pi$ and $^4\Sigma$ determinants and the assumption of a $^4\Phi$ ground state lead to the following expressions for the d–d transition energies:

$$^4\Phi \rightarrow {}^4\Sigma(\pi^2\sigma) = 7.5B — \tfrac{1}{2}(4E_1^2 — 36E_1B + 225B^2)^{\frac{1}{2}}$$

$$^4\Phi \rightarrow {}^4\Pi(\delta\pi\sigma) = 7.5B + \tfrac{1}{2}E_2 — \tfrac{1}{2}(E_2^2 + 6E_2B + 225B^2)^{\frac{1}{2}}$$

$$^4\Phi \rightarrow {}^4\Delta(\delta\pi^2) = E_2 — E_1$$

$$^4\Phi \rightarrow {}^4\Sigma(\delta^2\sigma) = 7.5B + \tfrac{1}{2}(4E_1^2 — 36E_1B + 225B^2)^{\frac{1}{2}}$$

$$^4\Phi \rightarrow {}^4\Pi(\delta^2\pi) = 7.5B + \tfrac{1}{2}E_2 + \tfrac{1}{2}(E_2^2 + 6E_2B + 225B^2)^{\frac{1}{2}}$$

The electronic spectrum of $CoCl_2$ in the gas phase[1,5] is dominated by an intense band, with much structure, at 14.2 kK. Weaker bands appear on the high energy side, at 18.2 kK, and on the low-energy side, at 10.4 kK. There is increasing absorption farther into the infra-red with a shoulder at 5.2 kK.

Two assignments have been proposed:

(A) Hougen *et al.*[1] assigned the intense band at 14.2 kK to the $^4\Phi \rightarrow {}^4\Sigma$ $(\delta^2\sigma)$ transition, while the band at 10.4 kK was assigned to $^4\Phi \rightarrow {}^4\Delta$. The infra-red absorption around 4 kK was attributed to the $^4\Phi \rightarrow {}^4\Pi$ $(\delta\pi\sigma)$ transition, while the $^4\Phi \rightarrow {}^4\Pi$ $(\delta^2\pi)$ transition was predicted to occur at high energy, *ca.* 30 kK where it would be masked by charge transfer absorption. The weak bands on the high energy side of the 14 kK band were assigned to doublet states.

(B) DeKock and Gruen[5] assigned the band at 18.2 kK to $^4\Phi \rightarrow {}^4\Pi$ $(\delta^2\pi)$ and the 14.2 kK band to $^4\Phi \rightarrow {}^4\Sigma$ $(\delta^2\sigma)$. The weak band around 10.4 kK was thought to be a component of the ^2G free-ion state and the absorption around 4 kK was assigned $^4\Phi \rightarrow {}^4\Delta$.

We shall now discuss these in turn. Assignment A was proposed by Hougen *et al.*[1] on the basis of a weak field scheme with neglect of any nephelauxetic effect and the assumption of splitting parameters as proposed by them for $CuCl_2$. Their calculated transition energies were in good agreement with those observed. However, if we assume in our strong-field approach that B is reduced to about 0.70 kK (as found[31] for $CoCl_4^{2-}$) a very different picture emerges. Attempts to fit the expressions given above for the transition energies $^4\Phi \rightarrow {}^4\Delta$ and $^4\Phi \rightarrow {}^4\Sigma$ to reasonable values of E_1 and E_2 give $E_1 \sim 11$ kK and $E_2 \sim 22$ kK, but predict a negative transition energy for $^4\Phi \rightarrow {}^4\Sigma$ $(\pi^2\sigma)$. In other words, such a large ligand field splitting leads to a $^4\Sigma$ $(\pi^2\sigma)$ ground state unless unreasonably high values of B, close to the free-ion value, are postulated. Assignment A must therefore be rejected. The possibility arises that the ground state is indeed $^4\Sigma$ $(\pi^2\sigma)$ but a closer examination suggests that this is unlikely. A detailed discussion of this point is presented in the Appendix.

Assignment B presents some problems too. DeKock and Gruen[5] allowed for a 14% reduction in the free-ion separation ^4P–^4F, but this would seem to be an underestimate. From the expressions given above for the transition energy $^4\Phi \rightarrow {}^4\Sigma$ $(\delta^2\sigma)$, we find values of E_1 in the range 11.2-11.4 kK for values of B in the range 0.65-0.75 kK. If the 18.2 kK band is assigned to the $^4\Phi \rightarrow {}^4\Pi$ $(\delta^2\pi)$ transition, E_2 is found to be in the range 9-11 kK. Thus a negative transition energy is predicted for $^4\Phi \rightarrow {}^4\Delta$, and for $^4\Phi \rightarrow {}^4\Sigma$ $(\pi^2\sigma)$. Indeed, $^4\Sigma$ $(\pi^2\sigma)$ should be the ground state, but we have already discarded this possibility for the reasons outlined in Appendix A. Asisgnment B cannot be easily upheld. We must therefore consider the possibility that the troublesome band at 14.2 kK is in fact due to some impurity, despite the fact that it is the most intense band in the d–d region. It is unlikely that it could be a band of the dimeric species Co_2Cl_4. This has been observed by mass spectrometry[32] but DeKock and Gruen[5] took great care to establish the absence of electronic transitions due to dimers in their spectra. However, Leroi *et al.*[2] assigned an infrared vibrational frequency in gaseous $CoCl_2$ to the dimer. A more probable source of impurity could be the $CoCl_2$ melt. Trutia and Musa[33] claimed that the spectra of Hougen *et al.*[1] included features of both the melt and the gas phase. Co^{II} in chloride melts[34,35] appears to assume a tetrahedral environment with an intense ($\varepsilon \sim 350$) band around 14 kK, assigned to the $^4A_2 \rightarrow {}^4T_1$ transition, as in $CoCl_4^{2-}$. The band at 18.2 kK does not appear in the melt. Gruen[36] considers it unlikely that his spectra of gaseous $CoCl_2$ were contaminated by the $CoCl_2$ melt since precautions were taken against this possibility; there is no evidence of such contamination in the spectra of the other dichlorides, comparing their spectra with those of the molten species,[37-39] although it must be borne in mind that the 14 kK band of molten $CoCl_2$ is much more intense than those of the other dichlorides and only a very small amount of the melt in the path of the incident light would affect the spectrum of gaseous $CoCl_2$.

We therefore suggest a different assignment to those previously given.[1,5] We ignore the 14.2 kK band and

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(34) A. Trutia and M. Musa, *Phys. Stat. Solidi 8*, 663 (1957).

(35) D. M. Gruen, *J. Ionrg. Nucl. Chem. 4*, 74 (1957).

(36) D. M. Gruen, private communication.

(37) D M. Gruen and R. L. McBeh, *Pure Appl. Chem. 6*, 23 (1963).

(38) D. M. Gruen and R. L. McBeth, *J. Phys. Chem. 66*, 57 (1962).

(39) D. M. Gruen and R. L. McBeth, *J. Phys. Chem. 63*, 395 (1959).

assign the 18.2 kK band to the ${}^4\Phi \rightarrow {}^4\Pi$ ($\delta^2\pi$) transition, and the weak 10.4 kK band to ${}^4\Phi \rightarrow {}^4\Sigma$ ($\delta^2\sigma$). The latter band may well correspond to the system observed[6] between 12.3 and 12.6 kK for $CoCl_2$ in an argon matrix at liquid helium temperature, and assigned[6] to a state arising from the ${}^4P$ term. An increase in energy of some 2 kK is not unreasonable over a temperature range of about 1000 deg. This assignment leads to much more satisfactory splitting parameters. In Table III we give value of E_1 and E_2 required to fit the transition energies with B in the range 0.65-0.75 kK. These are seen to be reasonable compared with the values found for $NiCl_2$ and they predict the transition ${}^4\Phi \rightarrow {}^4\Delta$ to occur around 4-5 kK, in agreement with the observed spectrum.

Table III. Splitting parameters and predicted transition energies for $CoCl_2$. All energies are in kK.

B	0.65	0.70	0.75
E_1	6.8	6.0	4.9
E_2	10.8	10.2	9.2
${}^4\Phi \rightarrow {}^4\Delta$	4.0	4.2	4.3

(d) *FeCl₂*. The d^6 configuration is a relatively simple one, and less equivocal assignments should be possible. The four-positron wave functions which represent the quintet states are:

$$(\delta_a\delta_b\pi_a\pi_b) = {}^5\Sigma$$
$$(\delta_a\pi_a\pi_b\sigma) = {}^5\Delta_a$$
$$(\delta_b\pi_a\pi_b\sigma) = {}^5\Delta_b$$
$$(\delta_a\delta_b\pi_a\sigma) = {}^5\Pi_a$$
$$(\delta_a\delta_b\pi_b\sigma) = {}^5\Pi_b$$

The strong field energies of these states, relative to the orbital energy of the configuration $\delta^4\ \pi^2$, and omitting the Racah parameter A, are:

$${}^5\Delta = E_2 - 21B$$
$${}^5\Pi = E_2 + E_1 - 21B$$
$${}^5\Sigma = 2E_2 - 21B$$

Assuming a ${}^5\Delta$ ground state, the d–d transition energies are simply:

$${}^5\Delta \rightarrow {}^5\Pi = E_1$$
$${}^5\Delta \rightarrow {}^5\Sigma = E_2$$

The spectrum[5] of gaseous $FeCl_2$ shows bands at 4.60 kK and 7.14 kK. Thus, assuming that $E_2 > E_1$, we find $E_1 = 4.6$ kK, $E_2 = 7.1$ kK.

(e) *CrCl₂*. The d^4 situations is analogous to the d^6 one discussed above. The four-electron wave functions of the quintet states are the same as the four-positron ones given for $FeCl_2$. The strong-field energies relative to the orbital energy of the configuration δ^4 are:

$${}^5\Sigma = 2E_1 - 21B$$
$${}^5\Pi = E_1 + E_2 - 21B$$
$${}^5\Delta = 2E_1 + E_2 - 21B$$

The d–d transition energies are given by:

$${}^5\Sigma \rightarrow {}^5\Pi = E_2 - E_1$$
$${}^5\Sigma \rightarrow {}^5\Delta = E_2$$

The spectrum of $CrCl_2$[5] shows bands at 5.4 kK and 9.0 kK. Thus $E_1 = 3.6$ kK and $E_2 = 9.0$ kK.

(f) *VCl₂*. The d^3 case is analogous to the d^7 configuration discussed above for $CoCl_2$. The three-electron wave functions of the quartet states are the same as the three-positron functions given for $CoCl_2$. The strong-field energies, relative to the orbital energy of the configuration δ^3, are:

$${}^4\Delta : 2E_1 - 15B$$
$${}^4\Phi : E_1 + E_2 - 15B$$

${}^4\Pi$	$\delta^2\pi$	$\delta\pi\sigma$
$\delta^2\pi$	$E_1 - 6B$	$3\sqrt{6}B$
$\delta\pi\sigma$	$3\sqrt{6}B$	$E_2 + E_1 - 9B$

${}^4\Sigma$	$\pi^2\sigma$	$\delta^2\sigma$
$\pi^2\sigma$	$2E_1 + E_2 - 3B$	$6B$
$\delta^2\sigma$	$6B$	$E_2 - 12B$

Taking the ground state to be ${}^4\Pi$ ($\delta^2\pi$), the d–d transition energies are:

$${}^4\Pi \rightarrow {}^4\Delta = E_1 - \tfrac{1}{2}E_2 - 7.5B + \tfrac{1}{2}(E_2^2 - 6E_2B + 225B^2)^{1/2}$$

$${}^4\Pi \rightarrow {}^4\Sigma(\delta^2\sigma) = \tfrac{1}{2}E_2 - \tfrac{1}{2}(4E_1^2 + 36E_1B + 225B^2)^{1/2} + \\ + \tfrac{1}{2}(E_2^2 - 6E_2B + 225B^2)^{1/2}$$

$${}^4\Pi \rightarrow {}^4\Phi = \tfrac{1}{2}E_2 - 7.5B + \tfrac{1}{2}(E_2^2 - 6E_2B + 225B^2)^{1/2}$$

$${}^4\Pi \rightarrow {}^4\Pi(\delta\pi\sigma) = (E_2^2 - 6E_2B + 225B^2)^{1/2}$$

$${}^4\Pi \rightarrow {}^4\Sigma(\pi^2\sigma) = \tfrac{1}{2}E_2 + \tfrac{1}{2}(4E_1^2 + 36E_1B + 225B^2)^{1/2} + \\ + \tfrac{1}{2}(E_2^2 - 6E_2B + 225B^2)^{1/2}$$

The spectrum of gaseous VCl_2[5] shows a relatively intense peak at 14.5 kK with a broad, structured absorption on the low-energy side with maxima at 9.6 kK and 10.7 kK. Two assignments are possible:

(A) DeKock and Gruen[5] assigned the 14.5 kK band to the ${}^4\Pi \rightarrow {}^4\Sigma$ ($\pi^2\sigma$) transition, and the absorption around 10 kK to the ${}^4\Pi \rightarrow {}^4\Pi$ transition.

(B) Alternatively, we might assign the 14.5 kK band to ${}^4\Pi \rightarrow {}^4\Pi$, and the 10 kK absorption to ${}^4\Pi \rightarrow {}^4\Sigma$ ($\pi^2\sigma$) transition at higher energy and masked by the intense charge transfer absorption beyond 20 kK.

First let us consider Assignment A. A major difficulty is the ill-defined position of the low-energy band. The peaks at 9.6 and 10.7 kK could be the spin-orbit components of the ${}^4\Pi$ state but this is not very likely since the spin orbit coupling constant for V^{2+} is only 0.19 kK. It seems most probable that the peak at 9.6 kK arises from a quartet state, while the sharper peak at 10.7 kK is due to a doublet state (${}^2\Delta$) superimposed on the broad envelope of the quartet band. We therefore solve the expressions for the d–d transition energies for E_1 and E_2, with ${}^4\Pi \rightarrow {}^4\Pi = 9.6$ kK and ${}^4\Pi \rightarrow {}^4\Sigma$ ($\pi^2\sigma$) $= 14.5$ kK. Values are calculated for values of B in the range 0.55 kK - 0.65 kK. This

(40) W. E. Smith, *J. Chem. Soc.* (*A*) 2677 (1969).

corresponds to a nephelauxetic effect comparable to that assumed for $CoCl_2$ and $NiCl_2$ and may be compared with the value of B of 0.615 kK found[40] for crystalline VCl_2. The results are shown in Table IV. E_1 and E_2 are seen to be rather small and some disturbing features arise. For low values of B, 0.55-0.60 kK, the $^4\Pi \rightarrow {}^4\Phi$ transition is predicted to appear around 4 kK, but the spectrum shows no absorption at this frequency. With higher values of B, we find that $E_1 > E_2$ and a $^4\Sigma$ ($\delta^2\sigma$) ground state is predicted.

Table IV. Splitting parameters and predicted transition energies for VCl_2 on the basis of Assignment A.

B	0.55	0.60	0.65
E_1	2.9	3.0	4.3
E_2	6.8	5.9	3.0
$^4\Pi \rightarrow {}^4\Delta$	0.2	0.4	2.7
$^4\Pi \rightarrow {}^4\Sigma(\delta^2\sigma)$	1.9	1.1	−1.9
$^4\Pi \rightarrow {}^4\Phi$	4.1	3.3	1.4

Table V. Splitting parameter E_2 and predicted transition energy $^4\Pi \rightarrow {}^4\Phi$ for VCl_2 on the basis of Assignment B. Energies in kK.

B	0.55	0.60	0.65
E_2	13.7	13.3	12.9
$^4\Pi \rightarrow {}^4\Phi$	10.0	9.8	9.5

We now turn to consider Assignment B. If we equate the expression for the $^4\Pi \rightarrow {}^4\Pi$ transition energy to 14.5 kK, we find values of E_2 for the various values of B as given in Table V. These values of E_2 give calculated transition energies for the $^4\Pi \rightarrow {}^4\Phi$ transition in good agreement with the observed absorption around 10 kK. Unfortunately, both these transitions are independent of E_1 and no other d–d bands are observed. However, E_1 must be around 7 kK if the $^4\Sigma$ ($\delta^2\sigma$) and $^4\Delta$ states are to lie sufficiently low in energy, and the $^4\Sigma$ ($\pi^2\sigma$) state sufficiently high in energy, to be unobserved. With $E_1 = 7.0$ kK and $B = 0.60$ kK, the $^4\Pi \rightarrow {}^4\Sigma$ ($\delta^2\sigma$) transition is predicted to appear at 3.4 kK, the $^4\Pi \rightarrow {}^4\Delta$ transition at 2.9 kK and the $^4\Pi \rightarrow {}^4\Sigma$ ($\pi^2\sigma$) transition at 24.2 kK. This would be consistent with the observed spectrum.

Assignment B therefore seems preferable. We shall return to the problem in the next section when we discuss the results of angular overlap calculations on the gaseous dichlorides.

Angular Overlap Calculations for Gaseous Dichlorides

We now attempt to calculate E_1 and E_2 for the compounds under consideration by means of the angular overlap model discussed above. In each case, we could find values of σ^* and π^* which yield the splitting parameters found by analysis of the spectrum. However, a more valuable exercise would be to calculate the covalence parameters in each case by reference to the ligand field splittings found in wellknown systems, *e.g.* MCl_4^{2-}. The procedure will be to determine the ratio $\sigma^*/(S^\sigma_{mx})^2 = \pi^*/(S^\pi_{mx})^2$ by analysis of the spectrum of such a system. By calculating the overlap integrals $S(3p_\sigma, 3d_\sigma)$ and $S(3p_\pi, 3d_\pi)$ at the appropriate internuclear distances, the covalence parameters for all the gaseous dichlorides can be found. The overlap integrals are calculated using the 3d-radial wave functions of Richardson *et al.*[41] for the M^+ ions and the functions of Clementi[42] for neutral chlorine. The crystal field parameters a_2 and a_4 are found from the wave functions of Richardson *et al.* for a charge of +0.5 on the metal, as suggested previously[10] for chlorocuprates(II).

It is necessary to make some assumptions regarding the metal-ligand bond lengths in the gaseous dichlorides. None of the compounds discussed has been the subject of a detailed structure determination. We assume that the M–Cl distance in each case is 0.20 Å shorter than in the corresponding MCl_4^{2-} ion, or 0.40 Å shorter than in crystalline MCl_2, in the absence of data for MCl_4^{2-}. These assumptions are based on the bond lengths found by electron diffraction[13] for other dichlorides compared with the corresponding distances in MCl_2 (cryst.) and MCl_4^{2-}. For example, $ZnCl_2$ (g) has a Zn–Cl distance of 2.05 Å, compared with ~2.26 Å in various tetrachlorozincates.[43-45] The variation in the M–Cl distance across the series should be similar in the gaseous dichlorides to that in the tetrachloride ions; the addition of electrons to the anti-bonding σ- and π-orbitals in MCl_2 should have a similar effect on bond lengths as the addition of electrons to the t_2 orbitals of the tetrahedral species.

(a) *$CuCl_2$.* We shall include here our previously reported[12] results for $CuCl_2$. In calculations on chlorocuprates(II) we have assumed $\sigma^*/S_\sigma^2 = \pi^*/S_\pi^2 = 170$ kK. This value has rationalised the d–d spectra of square coplanar, tetragonal octahedral, trigonal bipyramidal and flattened tetrahedral geometries. The mean Cu–Cl distance as found in Cs_2CuCl_4[46,47] is 2.22 Å. We therefore take the Cu–Cl distance in $CuCl_2$ (g) to be 2.02 Å. At this distance, $S^\sigma_{mx} = 0.100$, $S_{mx}^\pi = 0.064$. Hence $\sigma^* = 1.70$ kK, $\pi^* = 0.70$ kK. The radial parameters $\langle r^2\rangle$ and $\langle r^4\rangle$ are 1.4 a_o^2 and 5.2 a_o^4 respectively so that a_2 and a_4 are found to be 1.51 kK and 0.38 kK respectively, taking q (the point charge on each chlorine atom) to be −0.25. The splitting parameters E_1 and E_2 are then found to be 18.9 kK and 8.1 kK. These values would be consistent with the assignment of the 9 kK band to the transition $^2\Sigma \rightarrow {}^2\Pi$, with the $^2\Sigma \rightarrow {}^2\Delta$ transition hidden under the intense 19 kK absorption. The calculated transition energies are certainly not consistent with the alternative assignment. If, instead of calculating σ^* and Π^* on the basis of our previous analysis of the spectra of other chlorocuprates, we find a value of the ratio $\sigma^*/(S^\sigma_{mx})^2 = \pi/(S^\pi_{mx})^2$ to fit the 9 kK band exactly, we find that if the band is assigned to the $^2\Sigma \rightarrow {}^2\Pi$ transition, the $^2\Sigma \rightarrow {}^2\Delta$ transition is predicted to appear at 15.8 kK, which is

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(41) J. W. Richardon, R. R. Powell, W. C. Nieupoort, and W. F. Edgell, *J. Chem. Phys.* 36, 1057 (1962).

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(44) H. P. Klug and L. Alexander, *J. Amer. Chem. Soc.* 66, 1056 (1944).

(45) B. Brehler, *Naturwiss.* 46, 69, 106, 554 (1959).

(46) L. Helmholz and R. F. Kruh, *J. Amer Chem. Soc.* 74, 1176 (1952)

(47) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.* 65, 50 (1961).

consistent with the observed spectrum. If, on the other hand, we assign the 9 kK band to the $^2\Sigma \rightarrow {}^2\Delta$ transition, the $^2\Sigma \rightarrow {}^2\Pi$ transition is predicted to occur at 5.1 kK where it should not have escaped detection. Thus the angular overlap theory strongly supports the original assignment of Hougen *et al.*[1] as regards the 9 kK band.

(b) *$NiCl_2$.* A convenient reference system in order to find the ratio $\sigma^*/(S^{\sigma}_{mx})^2$ is tetrahedral $NiCl_4^{2-}$. X-ray analyses[48,49] give a metal-ligand distance of 2.27 Å in $NiCl_4^{2-}$, so we assume a distance of 2.07 Å in gaseous $NiCl_2$. Analysis of the d–d spectrum of $NiCl_4^{2-}$ indicates[29] a tetrahedral splitting parameter Δ_t of 3.6 kK. Our theoretical model expresses this splitting of the e and t_2 orbitals in a tetrahedral complex as:

$$\Delta_t = (20/3)\sigma^* - (80/9)\pi^* + (20/27)a_4$$

At 2.27 Å, $S^{\sigma}_{mx} = 0.089$ and $S^{\pi}_{mx} = 0.047$. $\langle r^4 \rangle$ for $Ni^{0.5+}$ is 6.5 a_o^4 so that a_4 (taking q to be 0.63) is 0.60 kK. Thus we find $\sigma^* = 0.72$ kK and $\pi^* = 0.20$ kK for $NiCl_4^{2-}$. This leads to $\sigma^*/(S^{\sigma}_{mx})^2 = \pi^*/(S^{\pi}_{mx})^2 = 91$ kK. At 2.07 Å, $S^{\sigma}_{mx} = 0.105$ and $S^{\pi}_{mx} = 0.063$. Thus for gaseous $NiCl_2$, $\sigma^* = 1.01$ kK and $\pi^* = 0.36$ kK. $\langle r^2 \rangle$ for $Ni^{0.5+}$ is 1.63 a_o^2 to that a_2 and a_4 for $NiCl_2$ are 1.49 kK and 0.38 kK respectively. Hence we obtain $E_1 = 4.7$ kK and $E_2 = 11.9$ kK. These values are seen to be in quite good agreement with those given in Table II, as found by analysis of the spectrum on the basis of Assignment B.

(c) *$CoCl_2$.* We proceed in exactly the same way as for $NiCl_2$. Tetrahedral $CoCl_4^{2-}$ has a Co–Cl distance of 2.28 Å,[50] so we take the bond lengths in $CoCl_2$ as 2.08 Å. The d–d spectra of tetrahedral tetrachlorocobaltates indicate[31] a splitting Δ_t of about 3.0 kK. At 2.28 Å, $S^{\sigma}_{mx} = 0.099$ and $S^{\pi}_{mx} = 0.054$. $\langle r^4 \rangle$ for cobalt is 8.3 a_o^4, leading to $a_4 = 0.67$ kK for $CoCl_4^{2-}$. Thus the observed splitting is accounted for by $\sigma^* = 0.62$ kK and $\pi^* = 0.19$ kK. This yields $\sigma^*/(S^{\sigma}_{mx})^2 = \pi^*/(S^{\pi}_{mx})^2 =$ 63 kK. At an internuclear distance of 2.08 Å, $S^{\sigma}_{mx} =$ 0.116 and $S^{\pi}_{mx} = 0.078$, so that $\sigma^* = 0.85$ kK and $\pi^* =$ 0.39 kK for $CoCl_2$. $\langle r^2 \rangle$ for cobalt is 2.07 a_o^2 so we obtain $a_2 = 1.87$ kK and $a_4 = 0.49$ kK. These parameters lead to $E_1 = 5.2$ kK,, $E_2 = 10.9$ kK for $CoCl_2$, in good agreement with the values quoted in Table III on the basis of the assignment proposed.

(d) *$FeCl_2$.* Tetrahedral $FeCl_4^{2-}$ would appear to be a convenient reference sysetm. The mean Fe–Cl distance is reported[51] as 2.31Å, so we assume a distance of 2.11 Å in gaseous $FeCl_2$. Unfortunately, we are confronted by some difficulties in determining Δ_t. Furlani *et al.*[52] quote a value of 4.0 kK, but this was based on the observation of a single band in a region where is much vibrational absorption from the cations present, and the presence of further d–d transitions at lower energy could not be excluded. This is important, because the X-ray analysis[51] showed an appreciable distortion from regular tetrahedral geometry, as we might expect from a d^6 system, and there is Mössbauer evidence [53,54] for appreciable splitting of the e orbitals. Thus the available spectroscopic data for $FeCl_4^{2-}$ cannot be easily analysed to yield the covalence parameters. An alternative course of action might be to invoke the useful 'rule of thumb' that the tetrahedral splitting Δ_t in MX_4^{2-} is usually very close to 0.5 of the octahedral splitting in crystalline MX_2. However, octahedral Fe^{II} systems show large band splittings[55-59] which may be caused by a Jahn-Teller distortion in the ^5E_g excited state. The electronic spectrum of solid $FeCl_2$[55] shows the $^5T_{2g} \rightarrow {}^5E_g$ transition split into components at 5.8 kK and 7.6 kK. Applying the analysis of Vechter,[59] it would seem that the lower-energy band best corresponds to the octahedral splitting Δ, so we estimate $\Delta_t = 2.9$ kK, a value more in line with those found for Co and Ni. S^{σ}_{mx} at 2.31 Å is 0.109 and S^{π}_{mx} is 0.061. $\langle r^4 \rangle$ for $Fe^{0.5+}$ is 10.8 a_o^4, leading to $a_4 = 0.96$ kK for tetrahedral $FeCl_4^{2-}$. Thus we find $\sigma^* = 0.51$ kK and $\pi^* = 0.16$ kK for $FeCl_4^{2-}$, giving $\sigma^*/(S^{\sigma}_{mx})^2 = \pi^*/(S^{\pi}_{mx})^2 = 43$ kK. At 2.11 Å, $S^{\sigma}_{mx} = 0.124$ and $S^{\pi}_{mx} = 0.086$. Thus for $FeCl_2$ we use $\sigma^* = 0.66$ kK, $\pi^* = 0.32$ kK. $\langle r^2 \rangle$ is 2.78 a_o^2, so that a_2 and a_4 for $FeCl_2$ are 2.40 kK and 0.57 kK respectively. We finally obtain $E_1 = 5.0$ kK, $E_2 = 9.6$ kK. These may be compared with the experimentally obtained values of 4.6 kK and 7.1 kK respectively. The agreement is not quite so good as for $CoCl_2$ and $NiCl_2$, but is reasonably satisfactory considering the assumptions involved.

(e) *$CrCl_2$.* In this case we are in even more serious difficulties in trying to determine the ratio $\sigma^*/(S^{\sigma}_{mx})^2$. Salts of $CrCl_4^{2-}$ have been made,[60] but no spectroscopic data is available. The anion is very probably a highly distorted tetrahedron, like $CuCl_4^{2-}$. If we assume that a hypothetical regularly tetrahedral $CrCl_4^{2-}$ ion had $\Delta_t \sim 3$ kK, comparable to the values found for other metals, we can proceed with the analysis. We take the Cr–Cl distance in our hypothetical ion to be 2.32 Å, with $S^{\sigma}_{mx} = 0.136$ and $S^{\pi}_{mx} = 0.084$. Thus we find $\sigma^*/(S^{\sigma}_{mx})^2 = \pi^*/(S^{\pi}_{mx})^2 = 27$ kK. At 2.12 Å, the internuclear distance assumed for gaseous $CrCl_2$, $S^{\sigma}_{mx} =$ 0.148 and $S^{\pi}_{mx} = 0.116$. These lead to $\sigma^* = 0.59$ kK and $\pi^* = 0.36$ kK for $CrCl_2$. With $a_2 = 2.9$ kK and $a_4 = 0.9$ kK, we obtain $E_1 = 5.8$ kK, $E_2 = 9.5$ kK, compared with the experimentally-determined values of 3.6 kK and 9.0 kK.

(f) *VCl_2.* No tetrachlorovanadate(II) has been reported, but the electronic spectrum of crystalline VCl_2 has recently[40] been the subject of a thorough study. On the basis that Δ_t for VCl_4^{2-} should be half of Δ for crystalline VCl_2, we would estimate $\Delta_t = 4.6$ kK.

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This seems rather high in comparison with the known tetrachlorides of the first row transition elements. We shall therefore assume a more representative value of $\Delta_t = 3.5$ kK for VCl_4^{2-}, and V–Cl bond length of 2.30 Å. With this internuclear distance, $S^{\sigma}_{mx} = 0.153$ and $S^{\pi}_{mx} = 0.103$. With $a_4 = 2.25$ kK, we find $\sigma^* = 0.67$ kK and $\pi^* = 0.30$ kK, leading to $\sigma^*/(S^{\sigma}_{mx})^2 = \pi^*/(S^{\pi}_{mx})^2 =$ 29 kK. At 2.10 Å, the distance assumed for gaseous VCl_2, $S^{\sigma}_{mx} = 0.162$ and $S^{\pi}_{mx} = 0.140$. Hence $\sigma^* = 0.76$ kK and $\pi^* = 0.57$ kK. With $a_2 = 3.2$ kK and $a_4 = 1.3$ kK, we obtain $E_1 = 7.8$ kK and $E_2 = 11.6$ kK, comparable with the values obtained by analysis of the spectrum on the basis of assignment B for VCl_2. It is difficult to see how the values of E_1 and E_2 consistent with Assignment A can be accounted for by theory.

Discussion

The angular overlap calculations give values of E_1 and E_2 in good agreement with the experimental splitting parameters for $NiCl_2$ and $CoCl_2$, but rather less satisfactory results for $FeCl_2$ and $CrCl_2$. For $CuCl_2$ and VCl_2 the results are reasonably good on the basis of assignments differing from those of DeKock and Gruen.[5] It is unwise to accept or reject a spectroscopic assignment solely on the basis of crude theoretical arguments; however, it does seem that the angular overlap method is a reasonable guide in deciding upon alternative assignments since it provides us with calculated ligand field splittings to within a couple of thousand wavenumbers in cases where there is enough data to permit the determination of the constant ratio $\sigma^*/(S^{\sigma}_{mx})^2$. The less satisfactory results for $FeCl_2$, $CrCl_2$, and VCl_2 are partly due to the lack of such data. Another important factor is that the crude point-charge model used to calculate the electrostatic conributions to the ligand field splitting is likely to be inadequate for the elements towards the left-hand side of the series, where the relatively diffuse d-orbitals lead to large values of a_2 and a_4. The inclusion of Madelung-like terms[61] in the MO treatment would lead to larger fractional charge on the metal atoms and consequently smaller crystal field terms. This might explain why our calculated values of E_1 and E_2 are consistently on the high side.

What is really significant about the results of the empirical calculations is that they help to rationalize trends in the observed values of E_1 and E_2 along the series. E_2 is seen to fall steadily along the series $CuCl_2 > NiCl_2 > CoCl_2 > FeCl_2$. This can be explained partly in terms of the decrease in the empirical constant $\sigma^*/(S^{\sigma}_{mx})^2$; but another important factor brought out by these calculations is the fact along this series, the d-orbitals become more diffuse and the contraction in the M–Cl bond length in going from MCl_4^{2-} to $MCl_2(g)$ leads to a smaller increase in S^{σ}_{mx}. But E_1 varies rather less along the series, and the ratio E_1/E_2 increases. This arises from the fact that S^{π}_{mx} still increases sharply with decreasing internuclear distance and the ratio $S^{\pi}_{mx}/S^{\sigma}_{mx}$ increases as the d-orbitals become more diffuse towards the left hand side of the series. The higher values of the splitting parameters in passing from $FeCl_2$ to $CrCl_2$ and VCl_2 is partly due to the large electrostatic contribution to the splitting at this end of the series, although the ratio $\sigma^*/(S^{\sigma}_{mx})^2$ seems to be increasing as well.

It is only fair to point out that in cases such as those discussed here, where we are applying the 'squared overlap' rule in comparing systems with very different internuclear distances, the results will be rather dependent on the exact form of the functions used. It is quite likely that the use of other wave functions, or other assumptions regarding fractional charges, would lead to significantly better (or worse) results. However, our simple treatment seems to give the correct general picture and we do not propose to speculate on possible refinements ot the method.

We should now include some further discussion of the assignments we have suggested for $CuCl_2$, $CoCl_2$, and VCl_2 as alternatives to those previously given. In the case of $CoCl_2$, reasonable values for E_1 and E_2 can only obtained by rejecting the 14.4 kK band and there are some legitimate grounds for doing so. In the case of $CuCl_2$, there seems to be ample scope for further argument. We tend to favour the assignment of the 9 kK band to the lower-energy d–d transition, $^2\Sigma \rightarrow {}^2\Pi$ with the $^2\Sigma \rightarrow {}^2\Delta$ transition lying around 16 kK, hidden under the intense 19 kK band. DeKock and Gruen[5] cited the E.S.R. studies of Kasai *et al.*[62] as further evidence for their assignment, which placed the $^2\Sigma \rightarrow {}^2\Pi$ transition below 4 kK. Kasai *et al.* studied the CuF_2 molecule in an argon matrix and estimated the $^2\Sigma \rightarrow {}^2\Pi$ transition in this molecule to be at 5.2 kK. They were unable to find any bands in the absorption spectrum at higher energy than 11 kK or lower than 5 kK; the near infra-red region was inaccessible. Since F^- is generally placed higher in the spectrochemical series than Cl^-, it would seem reasonable to suppose that the $^2\Sigma \rightarrow {}^2\Pi$ transition would be at ca. 4 kK in $CuCl_2$ with the $^2\Sigma \rightarrow {}^2\Delta$ transition at 9 kK. However, a closer study reveals that the results for CuF_2 are quite well accounted for on the basis of our model. An electron diffraction study of ZnF_2[63] gave a bond length of 1.81 Å. This is only 0.22 Å less than the Zn–F distance in crystalline ZnF_2,[64] compared with a reduction of 0.50 Å comparing crystalline $ZnCl_2$ with gaseous $ZnCl_2$. This is not at all surprising, since steric effects on bond lengths will be much less with fluoride ligands than with chloride. Thus the Cu–F distance in molecular CuF_2 is likely to be ca. 1.80 Å, probably a little shorter than in ZnF_2. Analysis of published[65,66] ligand field spectra of copper(II)-fluorine systems by our method inducates a value for $\sigma^*/(S^{\sigma}_{mx})^2$ of *ca.* 100 kK. At an internuclear distance of 1.80 Å, $S^{\sigma}_{mx} = 0.098$ and $S^{\pi}_{mx} = 0.055$, which leads to $\sigma^* = 0.96$ kK and $\pi^* =$ 0.30 kK for molecular CuF_2. We would then predict d–d transition energies of about 11 kK for $^2\Sigma \rightarrow {}^2\Delta$ and about 7 kK for $^2\Sigma \rightarrow {}^2\Pi$, consistent with the observations of Kasai *et al.*[62] It is of some interest to note at this point that the spectrochemical series for

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halide ligands with Cu^{II} (in so far as the series has much meaning for grossly non-cubic systems) appears to run in the reverse order to that found for most metals: chlorocuprates appear to have larger ligand field splittings than fluorocuprates, and the d–d transitions of trigonal bipyramidal $CuBr_5^{3-}$ have recently been shown[67] to lie at higher energy than in $CuCl_5^{3-}$.

In the case of VCl_2, the angular overlap calculations certainly favour Assignment B and there are other reasons, as outlined previously, for rejecting Assignment A. We feel that the results of such calculations can offer useful evidence for or against a particular assignment, but further corroboration is required. Infra-red studies on VCl_2 would help to settle the point.

Appendix

The possibility of a $^4\Sigma(\pi^2\sigma)$ ground state in $CoCl_2$.

If the ground state in $CoCl_2$ is assumed to be $^4\Sigma(\pi^2\sigma)$, the following d–d transition energies are predicted:

$$^4\Sigma \rightarrow {}^4\Phi = -7.5B + \tfrac{1}{2}(4E_1^2 - 36E_1B + 225B^2)^{1/2}$$

$$^4\Sigma \rightarrow {}^4\Delta = E_2 - E_1 - 7.5B + \tfrac{1}{2}(4E_1^2 - 36E_1B + 225B^2)^{1/2}$$

$$^4\Sigma \rightarrow {}^4\Pi(\delta\pi\sigma) = \tfrac{1}{2}E_2 - \tfrac{1}{2}(E_2^2 + 6E_2B + 225B^2)^{1/2} + \\ + \tfrac{1}{2}(4E_1^2 - 36E_1B + 225B^2)^{1/2}$$

$$^4\Sigma \rightarrow {}^4\Pi(\delta^2\pi) = \tfrac{1}{2}E_2 + \tfrac{1}{2}(E_2^2 + 6E_2B + 225B^2)^{1/2} + \\ + \tfrac{1}{2}(4E_1^2 - 36E_1B + 225B^2)^{1/2}$$

$$^4\Sigma \rightarrow {}^4\Sigma(\delta^2\sigma) = (4E_1^2 - 36E_1B + 225B^2)^{1/2}$$

An essential condition that $^4\Sigma(\pi^2\sigma)$ should be the ground state is that the transition energy $^4\Sigma(\pi^2\sigma) \rightarrow {}^4\Phi$ should be positive, and this will be so only if $E_1 > 9B$.

The assumption of a $^4\Sigma(\pi^2\sigma)$ ground state leads to three plausible assignments:

(A) The 18.2 kK band is assigned to the $^4\Sigma \rightarrow {}^4\Sigma(\delta^2\sigma)$ transition: the $^4\Sigma(\delta^2\pi)$ state lies at higher energy and is unobserved, and the 14.4 kK band is assigned to the $^4\Sigma(\pi^2\sigma) \rightarrow {}^4\Pi(\delta\pi\sigma)$ transition.

(B) The 14.4 kK band corresponds to the $^4\Sigma \rightarrow {}^4\Sigma(\delta^2\sigma)$ transition and the 18.2 kK band to the $^4\Sigma \rightarrow {}^4\pi(\delta^2\pi)$ transition.

(C) The $^4\Sigma(\delta^2\sigma)$ state is at 10.4 kK and the $^4\pi(\delta^2\pi)$ state at 18.2 kK. the 14.2 kK band is ignored, as discussed in the main text.

Assignment A, with the assumption of B in the range 0.65-0.75 kK, leads to $E_1 \sim 11$ kK and $E_2 \sim 22$ kK. However, the $^4\Sigma \rightarrow {}^4\Pi(\delta\pi\sigma)$ transition is predicted to appear at ~7 kK, where no absorption is observed. The assignment is therefore inconsistent with the spectrum as a whole.

Assignment B leads to $E_1 \sim 9$ kK and $E_2 \sim 8$ kK. It seems unreasonable to propose $E_2 < E_1$.

Assignment C requires that $E_1 < 9B$ which is incompatible with a $^4\Sigma(\pi^2\sigma)$ ground state.

We therefore conclude that a $^4\Sigma(\pi^2\sigma)$ ground state is improbable.

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