(10) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4736 (1961).
(11) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 2673 (1956).
(12) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953).
(13) pn:en or *i*-bn:en are ratios of specific rate constants at 25° for first-stage aquation of the analogous diamine systems indicated.
(14) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).
(15) A. D. Liehr, *J. Phys. Chem.*, **68**, 3629 (1964).
(16) It has been suggested [M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972)] that similar reasoning can explain the threefold decrease in the aquation rate of *trans*-Co(dan)$_2$Cl$_2^+$ relative to *trans*-Co(tn)$_2$Cl$_2^+$, where the *gem*-dimethyl groups restrict the distortion from the favored chair six-membered ring configuration.

Contribution from Chemistry Department I (Inorganic Chemistry),
H. C. Orsted Institute, DK-2100 Copenhagen O, Denmark

Electron Spin Resonance Spectra of Tetragonal Chromium(III) Complexes. II.[1] Frozen-Solution and Powder Spectra of $[Cr(NH_3)_5X]^{n+}$. A Correlation with Zero-Field Splittings and *g* Factors Obtained from Complete d^3-Configuration Calculations.

ERIK PEDERSEN* and SOLVEIG KALLESOE

Received March 11, 1974 AIC40165V

The X-band esr spectra have been recorded for complexes of the type $[Cr(NH_3)_5X]^{n+}$ where X = F$^-$, Cl$^-$, Br$^-$, I$^-$, H$_2$O, and OH$^-$. The complexes were in frozen solutions or diluted in the corresponding cobalt(III) complexes. All halide complexes showed tetragonal symmetry in frozen solutions. Small rhombic distortions were found in the hydroxo complex and in some halide complexes in polycrystalline powders. The zero-field splittings are in the range 0.06–0.94 cm^{-1}. The *g* factors are close to 1.99 and almost isotropic. These values have been compared with theoretical calculations based on all 120 states of the d^3 configuration, ligand field and interelectronic repulsion parameters obtained from vis–uv spectra, and the free-ion spin–orbit coupling constant. The zero-field splittings calculated in this way are very different from those obtained *via* simple second-order perturbation calculations including the lowest quartet and doublet states. The *g* factors calculated by the two methods differ only slightly. Thereby much better agreement with the experimental zero-field splittings has been obtained for the complexes with nonheavy ligands. Evidence for increased spin–orbit coupling constants in iodo and bromo complexes is found as also predicted by simple molecular orbital calculations. The experimental *g* factors, however, can only be explained by assuming all complexes to have spin–orbit coupling constants reduced to approximately 70% of the free-ion values.

Introduction

In a current investigation of the esr spectra of tetragonal chromium(III) complexes we have previously discussed the two series *trans*-$[Cr(NH_3)_4XY]^{n+}$ and *trans*-$[Cr(py)_4XY]^{n+}$ where X and Y are halide, water, or hydroxo ligands.[1] All these complexes showed essencially tetragonal symmetry, only slightly distorted by rhombic fields introduced by water and hydroxo ligands or in some cases by lattice effects in the polycrystalline powders. The tetragonal zero-field splittings were found to be in good agreement with complete d^3-configuration calculations based on parameters obtained from vis–uv absorption spectra. The free-ion value of the spin–orbit coupling constant was found satisfactory except for bromo and iodo complexes, for which increased values were required.

The present work extends this investigation to the pentaamminechromium(III) complexes and thereby exhausts the present sources of complexes having ideal symmetries and sufficiently well-determined ligand field and interelectronic repulsion parameters. During the preparation of this article another paper dealing with the esr spectra of the same series of complexes has appeared.[2] This investigation included the aqua-, chloro-, and bromopentaamminechromium(III) complexes in the microcrystalline state and agreed with our results for the chloro and bromo complexes.

Previous investigations of the kind discussed here have been made on systems exhibiting lower symmetry;[3-6] in the theoretical calculations most of the excited states have generally been neglected.[3,4,7-12] One of the exceptions is the calculation of the zero-field splitting of the ground states in ruby.[13-15] In this system the chromium(III) ions are in a trigonal environment. The breakdown of Van Vleck's theory[7] of zero-field splittings in axial symmetry is therefore obvious because of configuration interaction *via* the ligand field between the ground states and some of the excited states. In tetragonal symmetry all the interactions between the ground states and the excited states take place *via* spin–orbit coupling as assumed by Van Vleck.[7] A more detailed discussion of the results of these earlier papers is found in part I of this series.[1]

Experimental Section

Preparations. All complexes were prepared according to literature methods.[16-25] The chromium complexes were syncrystallized with the corresponding cobalt complexes from aqueous solutions containing 0.5% of chromium relative to cobalt. The chromium contents in the precipitates were not analyzed. Chlorides, bromides, perchlorates, and dithionates were investigated. Change of anions was generally found to have only small influence on the esr spectra. Due to the rapid hydrolysis of the iodopentaamminechromium(III) ion, even in acid solution, all spectra of this complex showed varying contamination with aquapentaammine complex. Frozen-solution spectra were measured on 10^{-2}–10^{-4} *M* solutions in a mixture of dimethylformamide, water, and methanol in the volume ratios 1:1:2. Solutions of aqua and hydroxo complexes were 10^{-2} *M* in H$^+$ and OH$^-$, respectively.

Esr Spectra. The spectra were recorded on a JEOL JES-ME-1X spectrometer, operating at the X band. The frequency was measured with a resonant cavity wavemeter with an accuracy of 1 MHz. The standard magnet pole gap was reduced by application of extra pole caps. The magnetic field thus obtained was 20–9000 G (2×10^{-3}–0.9 T). The field calibration below 2000 G was performed with a Hall probe gaussmeter with an accuracy of 1 G. Above 2000 G a sample of oxygen at 0.7 Torr was used as a reference having very narrow peaks at small intervals throughout the field range. Their positions and frequency dependencies have been carefully measured by Tinkham and Strandberg.[26] The accuracy of the field measurements in this range is thus determined by the wavemeter. All spectra were recorded by using 100-kHz field modulation. Amplitudes of 5 G were used for the powder spectra. For the frozen-solution spectra, having much broader lines, amplitudes of 10–20 G were used. The powder spectra were recorded at room temperature, and the frozen-solution spectra at −150°.

Discussion of the Esr Spectra

All spectra could be interpreted in terms of the spin Hamiltonian

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D[S_z^2 - {}^1\!/_3 S(S + 1)] + E(S_x^2 - S_y^2) \tag{1}$$

for $S = {}^3\!/_2$. The shape of the random orientation spectra, the computer simulation, and the procedure of fitting the spin Hamiltonian parameters have been discussed previously.[1] A characteristic selection of the experimental spectra of the polycrystalline powders is shown in Figure 1. An example of the similarity between the experimental and the simulated spectra is shown in Figure 1c and d. All frozen-solution spectra were similar to the powder spectra, except for their 2–10 times larger line widths. The parameters obtained from the spectra in terms of eq 1 are given in Table I.

$g_\parallel$ and $g_\perp$ were in all cases in the interval 1.98–1.99. The anisotropies were less than 0.01. Due to line widths of 50 G or more the g factors could not be determined accurately enough to allow a correlation with the theoretical anisotropies. All complexes have axial symmetry, only in some cases slightly distorted by rhombic fields. We therefore assume that the experimental D values may be correlated with the tetragonal ligand fields introduced by the halide or oxygen ligators. This assumption was valid for the trans complexes.[1] There is, however, at present no conclusive evidence from single-crystal esr spectra and X-ray structures.

The spin Hamiltonian parameters are almost unaffected by variations in the surrounding media. Fluoro complexes are exceptions to this, however. Their spectra are sometimes complicated by having very many lines. This has also been observed for *trans*-difluorotetraamminechromium(III) complexes.[1] In the fluoropentaamminecobalt(III) dithionate lattice we interpret this in terms of the presence of chromium complexes in different sites, giving rise to different D and E values.

Calculations of D, $g_\parallel$, and $g_\perp$

The application of complete diagonalizations of the energy matrices of the d^3 configuration in the presence of a tetragonal ligand field and a zero magnetic field has been discussed previously.[1,13-15] The computer program developed by Harnung and Monsted[27] has now been expanded to include the Zeeman effect.

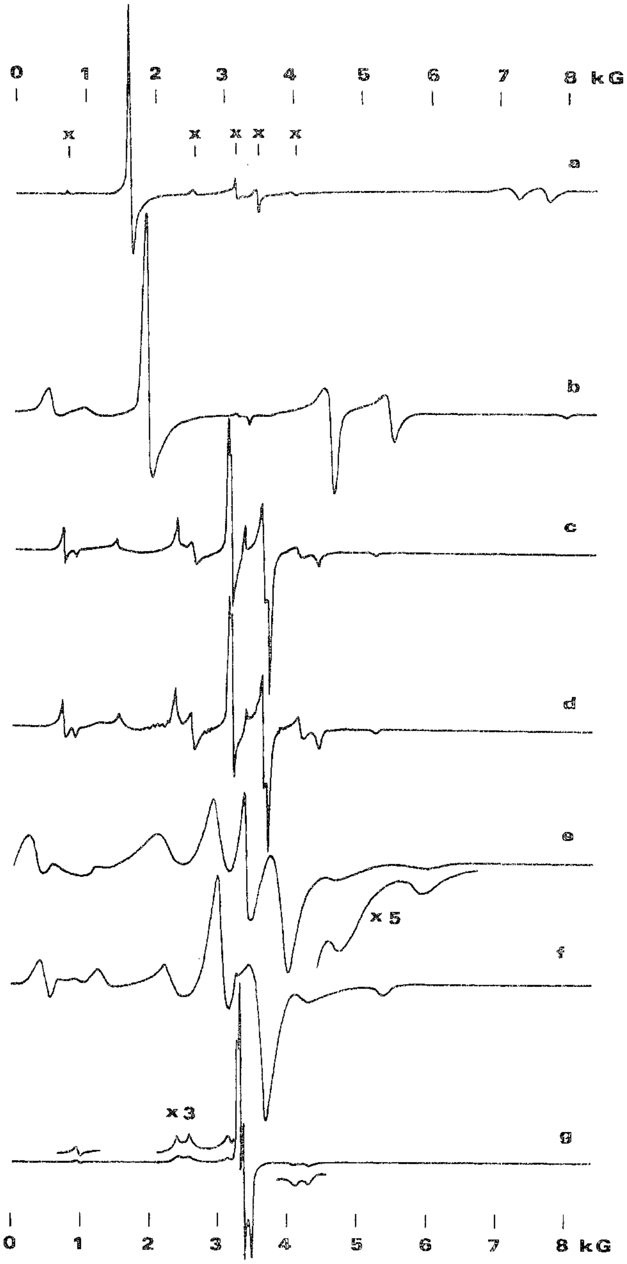

Figure 1. (a) Esr spectrum of 0.5% $[Cr(NH_3)_5I]^{2+}$ in $[Co(NH_3)_5I](ClO_4)_2$ at 9.443 GHz. The peaks marked with "x" are due to the presence of $[Cr(NH_3)_5H_2O]^{3+}$, formed by hydrolysis of the iodo complex. (b) Esr spectrum of 0.5% $[Cr(NH_3)_5Br]^{2+}$ in $[Co(NH_3)_5Br]Br_2$ at 9.446 GHz. (c) Esr spectrum of 0.5% $[Cr(NH_3)_5Cl]^{2+}$ in $[Co(NH_3)_5Cl]Cl_2$ at 9.445 GHz. (d) Computer-simulated spectrum assuming $g_x = g_y = g_z = 1.990$, $D = 0.087$ cm^{-1}, $E = 0.0042$ cm^{-1}, and a frequency of 9.445 GHz. Single-molecule spectra with lorentzian line widths of 50 G were integrated over all orientations by summation for each step of 1° in the polar angles Θ and Φ. (e) Esr spectrum of 1% $[Cr(NH_3)_5F]^{2+}$ in $[Co(NH_3)_5F](ClO_4)_2$ at 9.442 GHz. (f) Esr spectrum of 0.5% $[Cr(NH_3)_5H_2O]^{3+}$ in $[Co(NH_3)_5H_2O](ClO_4)_3$ at 9.223 GHz. (g) Esr spectrum of 0.5% $[Cr(NH_3)_5OH]^{2+}$ in $[Co(NH_3)_5OH](ClO_4)_2$ at 9.446 GHz.

A detailed analysis of the ligand field and interelectronic repulsion parameters of the pentaamminechromium(III) complexes is not available. One of the reasons for this is that the quartet → quartet transitions in the vis–uv region do not give sufficient information. Referring to the octahedral parentage functions the observed transitions are ${}^4A_2(t_2{}^3) \rightarrow {}^4T_2(t_2{}^2e)$ and ${}^4A_2(t_2{}^3) \rightarrow {}^4T_1(t_2{}^2e)$. Tetragonal splittings of the ${}^4T_1(t_2{}^2e)$ states are not observed. The three symmetry-required ligand field parameters can therefore not all be obtained directly. Quartet → doublet transitions at low temperatures may give this information and an estimate of the spin–orbit coupling constant. According to the angular overlap model the ligand field matrix elements consist of additive contributions from each central atom–ligand bond.[28] The tetragonal ligand field parameters Δe and Δt_2, defined according to Glerup and Schaffer,[29] are consequently for the pentaammines expected to have half the values they have in the corresponding *trans*-tetraammine complexes.[29] In our calculations we use Δe and Δt_2 derived in this way and values of Δ_{av} (the octahedral ligand field splitting), B, and C (Racah interelectronic repulsion parameters) obtained from the vis–uv absorption spectra of aqueous solutions of the complexes. $C = 5B$ was found to give reasonable values of the calculated energies of lowest doublets of the $t_2{}^3$ configuration. The free-ion value of the spin–orbit coupling constant $\zeta = 273$ cm^{-1} was used. The complete energy matrix of order 120 for the d^3 configuration was then diagonalized according to the procedure developed by Harnung and Monsted[27] for external

Table I. Spin Hamiltonian Parameters for Pentaamminechromium(III) Complexes[a]

Complex	Medium	$\lvert D\rvert$, cm^{-1}	$\lvert E\rvert$, cm^{-1}
$[Cr(NH_3)_5I]^{2+}$	$[Co(NH_3)_5I](ClO_4)_2$	0.469 ± 0.002	<0.001
	DMF-H_2O-MeOH, 10^{-2} *M* H^+	0.45 ± 0.01	<0.005
$[Cr(NH_3)_5Br]^{2+}$	$[Co(NH_3)_5Br]Br_2$	0.208 ± 0.002	<0.001
	DMF-H_2O-MeOH, 10^{-2} *M* H^+	0.20 ± 0.01	<0.005
$[Cr(NH_3)_5Cl]^{2+}$	$[Co(NH_3)_5Cl]Cl_2$	0.087 ± 0.001	0.0042 ± 0.002
	DMF-H_2O-MeOH	0.09 ± 0.01	<0.01
$[Cr(NH_3)_5F]^{2+}$	$[Co(NH_3)_5F](ClO_4)_2$	0.120 ± 0.005	<0.005
	$[Co(NH_3)_5F]S_4O_6$[b]	0.060 ± 0.002[b]	<0.002[b]
	DMF-H_2O-MeOH	0.12 ± 0.01	<0.01
$[Cr(NH_3)_5H_2O]^{3+}$	$[Co(NH_3)_5H_2O](ClO_4)_3$	0.080 ± 0.005	<0.005
	$[Co(NH_3)_5I](ClO_4)_2$	0.069 ± 0.001	<0.001
	DMF-H_2O-MeOH, 10^{-2} *M* H^+	0.08 ± 0.01	<0.01
$[Cr(NH_3)_5OH]^{2+}$	$[Co(NH_3)_5OH](ClO_4)_2$	0.043 ± 0.001	0.010 ± 0.002
	DMF-H_2O-MeOH, 10^{-2} *M* OH^-	0.030 ± 0.005	0.005
$[Cr(NH_3)_6]^{3+}$	DMF-H_2O-MeOH	<0.003	<0.001

[a] All *g* factors were in the range 1.98–1.99 with anisotropies less than 0.01. [b] The spectra show that the chromium complex occupies three different sites in this lattice. The sites introduce different *D* and *E* values. Parameters for one of the sites are given. Ambiguities in the assignments of some of the lines prevent us from getting accurate values for the other sites, but their *D* values are between 0.06 and 0.12 cm^{-1}.

Table II. Spin Hamiltonian Parameters Obtained from Complete d^3-Configuration Calculations and the Parameters Mentioned in the Text[a]

Complex	Δ_{av}	Δ_e	Δt_2	B	C	ζ	D	$g_\parallel$	$g_\perp$
$[Cr(NH_3)_5I]^{2+}$	18,900	2750	−250	630	3150	273	0.144	1.966	1.963
$[Cr(NH_3)_5Br]^{2+}$	19,100	2250	−500	635	3175	273	0.128	1.966	1.962
$[Cr(NH_3)_5Cl]^{2+}$	19,500	1500	−1000	640	3200	273	0.110	1.966	1.962
$[Cr(NH_3)_5F]^{2+}$	20,500	−500	−1750	660	3300	273	0.048	1.966	1.964
$[Cr(NH_3)_5H_2O]^{3+}$	20,800	750	−1000	650	3250	273	0.067	1.968	1.966
$[Cr(NH_3)_5OH]^{2+}$	19,700	−1750	−2250	650	3250	273	0.022	1.966	1.964

[a] All energy units are in cm^{-1}.

magnetic fields $H = 0$ and $H = 10{,}000$ G in directions parallel and perpendicular to the tetragonal symmetry axis. The accuracies of the energies obtained are $\pm 5 \times 10^{-4}$ cm^{-1}. Calculations for $H = 0$ directly give the zero-field splittings ($2D$ for the octahedral $^4A_2$ ground state). The validity of the spin Hamiltonian, eq 1, was controlled by several calculations using the parameters in Table II and magnetic fields up to 10^5 G. Within the accuracy of our diagonalizations it was always possible to describe the field and angular dependencies of the splittings of the ground states in terms of eq 1. Analytical expressions for the eigenvalues of the spin Hamiltonian exist for orientations of the magnetic field parallel to the magnetic axes.[30] These expressions were used for the calculation of $g_\parallel$ and $g_\perp$. The assumed parameters and the theoretically calculated spin Hamiltonian parameters are given in Table II.

Correlations with Experiments

Zero-Field Splittings. A comparison between Tables I and II demonstrates resonable agreements between theoretical and experimental zero-field splittings in hydroxo, aqua, fluoro (one of the sites in the dithionate lattice), and chloro complexes. The results of calculations based on restricted sets of basis functions, including the work in ref 2 (a corrected version of ref 12) have been discussed in ref 1. It is impossible to give a rigorous discussion of the uncertainties of the theoretical zero-field splittings based on uncertainties of the applied parameters, as the latter can only be crudely estimated. The zero-field splitting is a smooth "well-behaved" function of the six parameters. This function has an almost linear dependence on Δe, Δt_2, B, and C, is inversly proportional to Δ_{av}, and is approximately proportional to ζ^2 for values of these parameters, relevant for pentaamminechromium(III) complexes. Based on estimated uncertainties of the ligand field and repulsion parameters the calculated D values are expected to have uncertainties of 25% or 0.01 cm^{-1}, whichever is greater.

The zero-field splitting of the fluoropentaamminechromium(III) complex has a pronounced dependence of the solvent. The ligand field parameters have been obtained *via* absorption spectra of aqueous solutions. It is therefore more realistic to compare the zero-field splitting found in the frozen solution. In this case the agreement is poor, as also found[1] for all fluoro complexes of the types *trans*-$[Cr(NH_3)_4FX]^{n+}$ and *trans*-$[Cr(py)_4FX]^{n+}$.

Increased spin–orbit coupling constants are required for bromo and iodo complexes in order to understand their large zero-field splittings. This was also found for the trans complexes.[1] The intense quartet → doublet transitions in the visible absorption spectra[25] are in accordance with this. Qualitative arguments for large ζ values in these complexes in particular can be obtained *via* primitive molecular orbital calculations, including the spin–orbit coupling effect in these heavy ligands. Application of the appropriate one-electron LCAO antibonding molecular orbitals as given by Garrett, *et al.*,[12] and second-order perturbation calculations within the octahedral $^4A_2$ and $^4T_2$ states gives

$$D = \frac{{}^4/_9\,[({}^3/_4 a_1{}^{M} e^{M} + {}^1/_4 b_1{}^{M} e^{M})\zeta^{M} + {}^1/_8 a_1{}^{L} e^{L} \zeta^{L}]^2}{E(^4\mathrm{E})} - \frac{{}^4/_9\,[b_1{}^{M} b_2{}^{M} \zeta^{M}]^2}{E(^4\mathrm{B}_2)} \qquad (2)$$

a_1, b_1, b_2, and e are the coefficients in the molecular orbital functions, consisting of linear combinations of normalized ligand and d orbitals with corresponding symmetries in D_4. Superscripts M and L indicate metal and ligand, respectively. In eq 2 we have assumed that the spin–orbit coupling effects from the nitrogen ligators are negligible. In case of no admixture of ligand orbitals eq 2 is, of course, equivalent to the classical expression derived by Van Vleck.[7] Assuming the ligand orbital coefficients to be small, then the influence of the heavy ligand can be separated into an additive contribution to D according to

$$D = \frac{{}^1/_9\, a_1{}^{L} e^{L} \zeta^{M} \zeta^{L}}{E(^4\mathrm{E})} \qquad (3)$$

With the spin–orbit coupling constants estimated by McClure[31] ($\zeta^{Br} = 2460$ cm^{-1} and $\zeta^{I} = 5060$ cm^{-1}) the discrepancy between the experimental and theoretical zero-field splittings of the

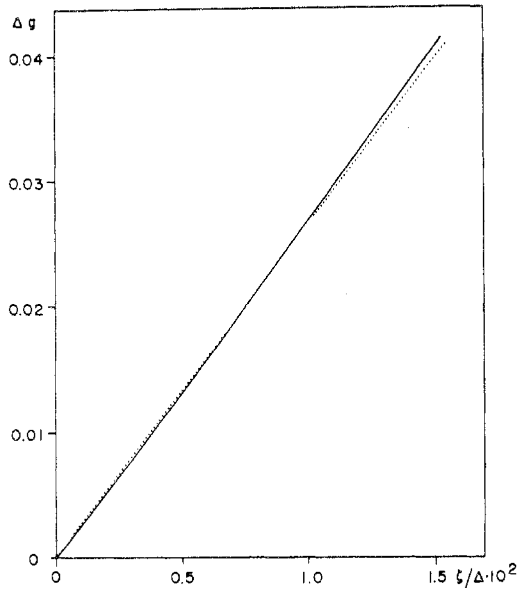

Figure 2. Complete calculations of $\Delta g = 2.0023 - g$ within the d^3 configuration in octahedral symmetry for $B = 675$ cm^{-1} and $C = 3200$ cm^{-1} (——). Δg is independent of variations of B and C within 100 and 500 cm^{-1}, respectively. The dotted line corresponds to $\Delta g = (8/3)(\zeta/\Delta)$ as obtained from second-order calculations neglecting all excited states except the $^4T_2$ states.

bromo and iodo complexes can be qualitatively explained by assuming that the unpaired electrons spend approximately 5% of their time in the halogen orbitals. This estimate was also made in the classical investigation of the esr spectra of the hexachloroiridate(IV) ion.[32,33] This kind of calculation should, however, be taken *cum grano salis* in view of the incompleteness and inadequacy of the energy matrix considered.

g Factors. The theoretically calculated g factors are in the range 1.962–1.968 with a maximum anisotropy of 0.004. The experimental values are all in the range of 1.98–1.99 with unaccurately determined anisotropies less than 0.01. This leaves the same problem as faced many times before in correlations with results of simplified calculations, including only interaction with the $^4T_2$ states, and leads to the assumption of reduced spin–orbit coupling constants. In fact, inclusion of all states of the d^3 configuration has very little influence on the calculated g factors, which in octahedral symmetry are[34]

$$g = 2.0023 - \frac{8}{3}\frac{\zeta}{\Delta} \tag{4}$$

Our calculated average g factors, $g_{av} = {}^1/_3(g_\parallel + 2g_\perp)$, are almost independent of Δe, Δt_2, B, and C. The ratio ζ/Δ_{av} turns out to be the only important parameter. The results are shown in Figure 2 for octahedral symmetry. All this seems to indicate that $^4T_2$ is the only excited level which has influence on the g factors. This simple behavior is only slightly modified by the presence of strong tetragonal distortions. The value of Δ_{av} is accurately determined from the vis–uv absorption spectra. Within the framework of the calculations we must therefore from the g factors conclude that the spin–orbit coupling constants are reduced rleative to their free-ion value.

The calculations predict very small anisotropies of the g factors. A comparison with experimental anisotropies can therefore not be based on random orientation esr spectra due to their considerable line widths.

Conclusion

In accordance with previous results[1] it has been found that the experimental zero-field splittings of the ground states in a series of tetragonal chromium(III) complexes can be satisfactorily understood in terms of complete d^3-configuration calculations using zeroth-order central atom basis wave functions, transforming as d functions, but incorporating adjustable ligand field and interelectronic repulsion parameters fitted to vis–uv absorption spectra. The free-ion spin–orbit coupling constant could be assumed for all complexes containing nonheavy ligands. The field dependencies of the ground states, predicted from such calculations including the Zeeman effect, agreed with a spin Hamiltonian description. However, the small Δg values obtained this way were in poor agreement with those obtained from the esr spectra. In order to account for the experimental g factors a reduction of the spin–orbit coupling constant to approximately 70% of the free-ion value is required. The fact that the zero-field splittings are proportional to ζ^2 therefore requires the tetragonal ligand field parameters to be approximately doubled, for example, or otherwise significantly changed. It may be too hasty at this point to conclude that the applied type of ligand field calculations are inadequate for the magnetic behavior of the ground states. But we have our doubts that such changes in the parameters can be incorporated in a coherent description of all the observable energy levels.

Acknowledgment. We are grateful to "Statens naturvidenskabelige forskningsrad" for provision of the esr spectrometer and to C. E. Schaffer and J. Glerup for valuable inspiration during this work. We are also indebted to S. E. Harnung and O. Monsted for the permission to use their computer programs for the diagonalization of the d^3-configuration energy matrix.

Registry No. $[Cr(NH_3)_5I]^{2+}$, 17979-08-7; $[Cr(NH_3)_5Br]^{2+}$, 22289-65-2; $[Cr(NH_3)_5Cl]^{2+}$, 14482-76-9; $[Cr(NH_3)_5F]^{2+}$, 19443-25-5; $[Cr(NH_3)_5H_2O]^{3+}$, 15975-47-0; $[Cr(NH_3)_5OH]^{2+}$, 22289-66-3; $[Co(NH_3)_5I](ClO_4)_2$, 15156-20-4; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5F](ClO_4)_2$, 15156-21-5; $[Co(NH_3)_5H_2O](ClO_4)_3$, 13820-81-0; $[Co(NH_3)_5OH](ClO_4)_2$, 18885-27-3; Cr, 74440-47-3.

References and Notes

(1) Part I: E. Pedersen and H. Toftlund, *Inorg. Chem.*, **13**, 1603 (1974).
(2) L. E. Mohrmann, Jr., and B. B. Garrett, *Inorg. Chem.*, **13**, 357 (1974).
(3) B. R. McGarvey, *J. Chem. Phys.*, **41**, 3743 (1964).
(4) J. C. Hempel, L. O. Morgan, and W. B. Lewis, *Inorg. Chem.*, **9**, 2064 (1970).
(5) J. M. Flowers, J. C. Hempel, W. E. Hatfield, and H. H. Dearman, *J. Chem. Phys.*, **58**, 1479 (1973).
(6) J. C. Hempel, D. Klassen, W. E. Hatfield, and H. H. Dearman, *J. Chem. Phys.*, **58**, 1487 (1973).
(7) J. H. Van Vleck, *J. Chem. Phys.*, **7**, 61 (1939).
(8) P. H. E. Meijer and H. J. Gerritsen, *Phys. Rev.*, **100**, 742 (1955).
(9) S. Sugano and M. Peter, *Phys. Rev.*, **122**, 381 (1961).
(10) H. Kamimura, *Phys. Rev.*, **128**, 1077 (1962).
(11) L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).
(12) H. B. Garrett, K. DeArmond, and H. S. Gutowsky, *J. Chem. Phys.*, **44**, 3393 (1966).
(13) R. M. Macfarlane, *J. Chem. Phys.*, **39**, 3118 (1963).
(14) R. M. Macfarlane, *J. Chem. Phys.*, **42**, 442 (1965).
(15) R. M. Macfarlane, *J. Chem. Phys.*, **47**, 2066 (1967).
(16) M. Linhard and W. Berthold, *Z. Anorg. Allg. Chem.*, **279**, 173 (1955).
(17) M. Linhard and M. Wiegel, *Z. Anorg. Allg. Chem.*, **278**, 24 (1955).
(18) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **20**, 105 (1879).
(19) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **25**, 83 (1882).
(20) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **31**, 49 (1885).
(21) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **25**, 418 (1882).
(22) S. M. Jorgensen, *J. Prakt. Chem.*, [2] **19**, 49 (1879).
(23) S. M. Jorgensen, *Z. Anorg. Chem.*, **19**, 79 (1899).
(24) M. Mori, *Inorg. Syn.*, **5**, 134 (1957).
(25) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **266**, 49 (1951).
(26) M. Tinkham and M. W. P. Strandberg, *Phys. Rev.*, **97**, 951 (1955).
(27) S. E. Harnung, O. Monsted, and E. Pedersen, to be submitted for publication.
(28) C. E. Schaffer and C. K. Jorgensen, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **34** (13), 1 (1965).
(29) J. Glerup and C. E. Schaffer, *Proc. Int. Conf. Coord. Chem.*, **11**, 500 (1968).
(30) B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).
(31) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
(32) J. H. E. Griffiths, J. Owen, and I. M. Ward, *Proc. Roy. Soc., Ser. A*, **219**, 526 (1953).
(33) J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc., Ser. A*, **226**, 96 (1954).
(34) W. G. Penney and R. Schlapp, *Phys. Rev.*, **42**, 666 (1932).