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Partial Quenching of Parametrical Tetragonality of a Chromium(III) Complex by Pressure Tuning[†]

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The ligand-field spectrum of $[Cr(NH_3)_4F_2]AsF_6$ has been pressure-tuned up to 100 kbar. The parametrical analysis shows that the absolute values of the two independent tetragonalities of the chromophoric ion both decrease with increasing isotropic pressure so that the molecular ion becomes more isotropic. Moreover, the Cr−N single bonds appear to be more compressible than the Cr−F bonds, for which it is parametrically clear that they have a partial multiple-bond character. While the spectrochemical parameter for F^-, Δ_F, increases with pressure, its two components $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ decrease. It is confirmed that nephelauxetism increases with pressure.

Introduction

The spectrochemical series of ligands bears the name of Tsuchida[1] and has been known from before ligand-field theory was used to rationalize it. This series depends roughly upon the ligating atoms[2] and can be sketched accordingly as

$$I < Br < Cl < F < O < N < C \qquad (1)$$

The ligand-field rationalization associated the series with increasing values of the empirical parameter Δ applying to cubic complexes. This parameter is defined by

$$\Delta \equiv h(e_g) - h(t_{2g}) \qquad (2)$$

where h refers to the orbital energies of the model and the symbols for the symmetry species to the octahedron. It was found that the series was the same for all central ions and that a spectrochemical series of constant ligand and varying central ions could likewise be established.[3]

For octahedral complexes the e_g orbitals are by symmetry able to form σ bonds with the ligands, but not π bonds, whereas the opposite symmetry conditions apply to the t_{2g} orbitals. Therefore, Δ was later written as

$$\Delta = \Delta_\sigma - \Delta_\pi \qquad (3)$$

and interpreted as the *difference* between a σ and a π antibonding energy (where Δ_π, however, could be negative in case the π interaction with the ligands made the t_{2g} orbitals net bonding rather than antibonding).

This interpretation contributed order to inorganic chemistry, especially after it turned out that all Δ values seemed to be positive (no negative Δ value having until now been found). This fact was in good agreement with chemical feeling and with computational experience that σ interactions supersede π interactions in energetic importance. There is therefore an almost unanimous view among inorganic chemists that Δ can be considered in this way.

On the other hand, the fact that Δ was a difference quantity made its numerical value less valuable chemically. Immediately, there seemed to be no solution to this problem because it is a parameter obtained from spectra of octahedral complexes, which only embody information about the single orbital energy difference represented by the empirical ligand-field parameter Δ of eq 2. One needs lower-symmetry complexes in order to obtain more orbital energy differences and thereby the possibility of determining the components of Δ according to eq 3.

For the kind of complexes that we are here discussing, that is, complexes which have valence angles of 90 and 180°, Yamatera[4] and McClure[5] invented a new parametrization of the ligand field which in principle allowed the spectrochemical series to be split into two new series: a σ and a π series. McClure[5] gave for the central ion cobalt(III) a preliminary proposal to the order of certain ligands in these new series for which he invented the following collective name: the two-dimensional spectrochemical series.

The complexes that we are here talking about were later called orthoaxial complexes,[6] and the additive ligand-field model of Yamatera and McClure was generalized to what is now called the angular overlap model (AOM).[7] This model, which can be used for any complex of any symmetry or even without symmetry, has a molecular-orbital version (MO-AOM) and a

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ligand-field version (LF-AOM).[8] Geometrical knowledge is the only prerequisite for setting up the theoretical part of the AOM. The rest of the use of the model is concerned with the model's radial parameters, which must be determined by comparison with experiment.

On the experimental side of the use of the LF-AOM, it turned out that it was extremely difficult to obtain data which allowed the determination of the empirical parameters required in order to establish the parameter values for the various ligands in the two-dimensional spectrochemical series. Actually, the task has up till now been reasonably successfully solved only for the central ion chromium(III) and only for a few ligands. The two parametrically independent series are[9]

$$\mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{OH_2} < \mathrm{NH_3} < \mathrm{F^-} < \mathrm{(OH)^-} \qquad \Delta_\sigma \text{ series}$$

$$\mathrm{NH_3} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{OH_2} < \mathrm{F^-} < \mathrm{(OH)^-} \qquad \Delta_\pi \text{ series} \quad (4)$$

It is seen that the series are the same except for the position of NH_3, which has no π electrons to contribute. This means, with the limited knowledge we have, that it is important for a ligand's behavior whether it has filled π orbitals or not. If it has such orbitals, they will overlap and interact with the orbitals of the central ion. This is in agreement with the extraordinary spectrochemical results that apply to ligands with sulfur as coordinating atom. These ligands cannot be placed in the series (1) in agreement with the fact that their number of filled π orbitals varies. For example, SO_3^{2-} which has no filled π orbitals on the sulfur has a high position in the spectrochemical series, around the same place as NH_3, whereas ^-SR has a low position, among the heavy halides.[10]

In the past when the ligand-field model was conceived as an electrostatic model, it provided an expectation for the dependence of Δ on the metal to ligator distance r. This fact served as an impetus for the study of the pressure dependence of Δ, which was made for several octahedral complexes.[11] The dependence found could be described as an approximate proportionality

$$\Delta \propto r^{p}, \quad p \approx -5 \text{ or } -6 \qquad (5)$$

This result could not have killed the electrostatic model. In fact, the event is an example of two interesting properties of models: they may inspire new experiments and they may provide predictions that turn out to be correct even if the model itself turns out to be distant from being physically realistic.

The result (5) contains quantitative knowledge regarding the empirical parameter Δ, which, as we saw above, is conceived as a difference quantity. It would therefore seem to be worthwhile to try to establish the pressure dependencies of its individual parts, the σ and π components, especially in view of the scarce knowledge we have about these parts. This problem is not a trivial one, either on the experimental side or on the conceptual side. The present paper is a first attempt at doing this. It sets out with the complex ion $[Cr(NH_3)_4F_2]^+$ which was the main contributor to the quantification of the series (4).[9] The ligand-field spectrum of $[Cr(NH_3)_4F_2]AsF_6$ was measured from atmospheric pressure to 100 kbar.

Holistic Tetragonal Ligand Fields and Orthoaxial Symmetry Hierarchy

In holistic, that is, nonadditive, ligand-field theory,[12] the molecular symmetry plus the restrictions that arise from the use of a function space limited to the five d functions governs the issue alone, and even though the ligands may have a conceptual individuality, their individual ligand fields do not. The holistic theory is useful because it allows one to decide how many independent ligand-field parameters a system of a given symmetry is able to provide within the model boundary conditions.

When the holohedric symmetry is tetragonal and belongs to the special hierarchy $O_h \supset D_{4h} \supset D_{2h}$ in which the two equivalent C_2 axes of D_{4h} which coincide with two of the C_4 axes of O_h are also two of the C_2 axes of D_{2h}, we have a situation where symmetry and geometry meet in a way that is important for "octahedral" complexes. We shall name this *symmetry–geometry hierarchy* the *orthoaxial hierarchy*.

In this hierarchy the tetragonal ligand field can be written in terms of mutually orthogonal parametric operators[12] if the relative orbital energies are defined by

$$\mathrm{b}_1(D_4): \quad h(x^2 - y^2) = {}^3/_5\Delta(\mathrm{d}) + {}^1/_2\Delta(\mathrm{e}) \qquad (6a)$$

$$\mathrm{a}_1(D_4): \quad h(z^2) = {}^3/_5\Delta(\mathrm{d}) - {}^1/_2\Delta(\mathrm{e}) \qquad (6b)$$

$$\mathrm{b}_2(D_4): \quad h(xy) = -{}^2/_5\Delta(\mathrm{d}) + {}^2/_3\Delta(\mathrm{t}_2) \qquad (6c)$$

$$\mathrm{e}(D_4): \quad h(yz) = h(zx) = -{}^2/_5\Delta(\mathrm{d}) - {}^1/_3\Delta(\mathrm{t}_2) \qquad (6d)$$

where $\Delta(\mathrm{d}) = \Delta$ now accounts for the average octahedral field and $\Delta(\mathrm{e})$ and $\Delta(\mathrm{t}_2)$ account for two parametrically independent tetragonal fields, a σ field and a π field, the octahedral property that the e orbitals have σ and the t_2 orbitals π symmetries (and not vice versa) being conserved because the $b_1(D_4)$ and $a_1(D_4)$ orbitals still have a pure $e(O)$ parentage and the $b_2(D_4)$ and $e(D_4)$ orbitals a pure $t_2(O)$ parentage. For these systems the parametrical ligand-field Hamiltonian then has the form

$$H_{\mathrm{LF}} = \Delta(\mathrm{d})\, \hat{Q}[\Delta(\mathrm{d})] + \Delta(\mathrm{e})\, \hat{Q}[\Delta(\mathrm{e})] + \Delta(\mathrm{t}_2)\, \hat{Q}[\Delta(\mathrm{t}_2)] \qquad (7)$$

where the operators that are coefficients of the parameters are mutually orthogonal, dimensionless entities, defined by eqs 6 and 7. For example, $\hat{Q}[\Delta(\mathrm{t}_2)]$ may alternatively be defined by the expression

$$\begin{array}{c|ccc} \hat{Q}[\Delta(\mathrm{t}_2)] & xy & yz & zx \\ \hline xy & {}^2/_3 & 0 & 0 \\ yz & 0 & -{}^1/_3 & 0 \\ zx & 0 & 0 & -{}^1/_3 \end{array} \qquad (8)$$

or if the usual real d function basis is understood, the matrix of

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(9) (a) Glerup, J.; Schäffer, C. E. In *Progress in Coordination Chemistry*; Cais, M., Ed.; Elsevier: Amsterdam, 1968; pp 500–502. (b) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399–1407. (c) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1980**, *19*, 2855–2857 and references therein.

(10) Jørgensen, C. K. *Inorganic Complexes*; Academic Press: New York, 1963.

(11) Drickamer, H. G.; Frank, C. W. *Electronic Transitions and High Pressure Chemistry and Physics of Solids*; Chapman and Hall: London, 1973; Chapter 6, pp 174–192 and references therein.

(12) (a) Brorson, M.; Damhus, T.; Schäffer, C. E. *Comments Inorg. Chem.* **1983**, *3*, 1–34. (b) Bendix, J.; Brorson, M; Schäffer, C. E. *Coord. Chem. Rev.* **1989**, *94*, 181–241 and references therein.

$\hat{Q}[\Delta(t_2)]$, $\boldsymbol{Q}[\Delta(t_2)]$, may be simply written as

$$\boldsymbol{Q}(\Delta(t_2)] = \begin{bmatrix} {}^2/_3 & 0 & 0 \\ 0 & -{}^1/_3 & 0 \\ 0 & 0 & -{}^1/_3 \end{bmatrix} \tag{9}$$

The norm square of the operator over the five d orbitals is found as the sum of the squares of its matrix elements.[12] For $\boldsymbol{Q}[\Delta(t_2)]$ we thus obtain

$$\langle \hat{Q}[\Delta(t_2)] | \hat{Q}[\Delta(t_2)] \rangle = \langle \boldsymbol{Q}[\Delta(t_2)] | \boldsymbol{Q}[\Delta(t_2)] \rangle = ({}^2/_3)^2 + (-{}^1/_3)^2 + (-{}^1/_3)^2 = {}^6/_9 = {}^2/_3 \tag{10}$$

and for the other norm squares we obtain similarly

$$\langle \hat{Q}[\Delta] | \hat{Q}[\Delta] \rangle = {}^6/_5 \tag{11a}$$

$$\langle \hat{Q}[\Delta(e)] | \hat{Q}[\Delta(e)] \rangle = {}^1/_2 \tag{11b}$$

Perhaps the most important consequence[12] of using *mutually orthogonal operators* is the fact that the *sum-square splitting* (s.sq.s.), that is, the sum of the squares of the energies of all the states on which the operator set acts, is equal to the sum of the squares of the parameters, each parameter being weighted by its coefficient operator's norm square. This means that the responsibility for the sum-square splitting can be quantitatively allocated to the individual ligand-field parameters. From eq 6 it is immediately clear that the two parametric cross products cancel when the sum-square splitting is calculated. It is also clear that the operators $\hat{Q}[\Delta(e)]$ and $\hat{Q}[\Delta(t_2)]$ are orthogonal since they act on two different subspaces of d space.

Let us anticipate our results by calculating from our experiments the three parametric contributions to the d orbital sum-square splitting in $[Cr(NH_3)_4F_2]AsF_6$ at atmospheric pressure. We find

$$\Delta = 1.900, \quad \Delta(e) = -0.215, \quad \Delta(t_2) = -0.412 \qquad (\text{all in } \mu\text{m}^{-1}) \tag{12}$$

With the norm squares ${}^6/_5$, ${}^1/_2$, and ${}^2/_3$ of the coefficient operators over the five-dimensional space of the d orbitals, we obtain

$$\Delta^2 \langle \hat{Q}[\Delta] | \hat{Q}[\Delta] \rangle = 4.33\ \mu\text{m}^{-2} \tag{13a}$$

$$[\Delta(e)]^2 \langle \hat{Q}[\Delta(e)] | \hat{Q}[\Delta(e)] \rangle = 0.023\ \mu\text{m}^{-2} \tag{13b}$$

$$[\Delta(t_2)]^2 \langle \hat{Q}[\Delta(t_2)] | \hat{Q}[\Delta(t_2)] \rangle = 0.113\ \mu\text{m}^{-2} \tag{13c}$$

which shows that the cubic part of the ligand field in this "octahedral" complex makes up 97% of the sum-square splitting and the two parametrically independent tetragonal fields accordingly 3%.

The Ligand Field Partitioned into Single-Ligand Contributions

The angular overlap model allows the ligand field to be partitioned so that the ligands provide their individual contributions to the splitting of the d orbitals and the global ligand field becomes a sum of these contributions.[7] This means that we must obtain empirical parameters which refer to these individual ligands when we compare the experimental spectra with the AOM expressions for the transition energies. It does not imply any assumption about transferability of such empirical parameters either from one complex to the other or from one ligand of the same kind to an other one within a given complex, unless these ligands are equivalent by symmetry. On the other hand, such transferabilities would of course be wonderful to find empirically, and they have in fact in some cases been found to apply extremely well.[9]

By using the AOM, one obtains the following expressions for the parameters of the holistic model applied to the complex ion $[Cr(NH_3)_4F_2]^+$:

$$\Delta(d) = \Delta = {}^1/_3(2\Delta_N + \Delta_F) = {}^1/_3(2\Delta'_N + \Delta'_F) \tag{14ai}$$

$$\Delta(e) = {}^2/_3(\Delta_{\sigma N} - \Delta_{\sigma F}) = {}^2/_3(\Delta'_{\sigma N} - \Delta'_{\sigma F}) \tag{14aii}$$

$$\Delta(t_2) = {}^1/_2(\Delta_{\pi N} - \Delta_{\pi F}) = -{}^1/_2\Delta'_{\pi F} \tag{14aiii}$$

where the parameters Δ_σ and Δ_π for linearly ligating ligands J are related to the AOM single-ligand parameters by the relations

$$\Delta_{\sigma J} = 3(e_{\sigma J} - e_{\delta J}) \tag{14bi}$$

$$\Delta_{\pi J} = 4(e_{\pi J} - e_{\delta J}) \tag{14bii}$$

and where, by definition

$$\Delta_J \equiv \Delta_{\sigma J} - \Delta_{\pi J} \tag{14c}$$

The expressions on the extreme right of eq 14a use $\Delta_{\pi N}$ as the zero point for the other parameters[9] as illustrated by the definitions

$$\Delta'_{\sigma F} \equiv \Delta_{\sigma F} - \Delta_{\pi N} \tag{15a}$$

$$\Delta'_{\pi F} \equiv \Delta_{\pi F} - \Delta_{\pi N} \tag{15b}$$

$$\Delta_F \equiv \Delta_{\sigma F} - \Delta_{\pi F} = \Delta'_{\sigma F} - \Delta'_{\pi F} \tag{15c}$$

With these definitions, the problem of going from the three-parameter holistic model to the four-parameter partitioned model has been overcome. On the other hand, the parameter $\Delta_{\pi N}$, which we take as our zero point because we expect it to be small from a chemical point of view, remains undetermined in our experiment.

The reverse of eq 14a may usefully be written as

$$\Delta'_{\sigma N} = \Delta(d) + {}^1/_2\Delta(e) - {}^2/_3\Delta(t_2) \tag{16a}$$

$$\Delta'_{\sigma F} = \Delta(d) - \Delta(e) - {}^2/_3\Delta(t_2) \tag{16b}$$

$$\Delta'_{\pi F} = -2\Delta(t_2) \tag{16c}$$

$$\Delta_N = \Delta'_{\sigma N} = \Delta(d) + {}^1/_2\Delta(e) - {}^2/_3\Delta(t_2) \tag{16d}$$

$$\Delta_F = \Delta(d) - \Delta(e) + {}^4/_3\Delta(t_2) \tag{16e}$$

The above mentioned results (eq 12) for $[Cr(NH_3)_4F_2]AsF_6$ at atmospheric pressure can then be given as

$$\Delta_N = \Delta'_{\sigma N} = 2.067, \quad \Delta_F = 1.566, \quad \Delta'_{\sigma F} = 2.390, \quad \Delta'_{\pi F} = 0.824 \qquad (\text{all in } \mu\text{m}^{-1}) \tag{17}$$

The remarkable thing is that F^-, which is a low-Δ ligand according to the quantification of expression 1, has a σ parameter, $\Delta'_{\sigma F}$, which is pronouncedly larger than that, $\Delta'_{\sigma N}$, applying to the high-Δ ligand NH_3. This result, which of course implies $\Delta_{\sigma F} > \Delta_{\sigma N}$ (cf. eq 15), is a parametric fact and a chemical consequence of the data transformation which the model allows one to make. This result gives an additional reason for finding it worthwhile to study the components of Δ_F, $\Delta'_{\sigma F}$ and $\Delta'_{\pi F}$, separately. How far the parameters will prove to make chemical sense will be a question for the future, but there is no doubt that the collection of empirical ligand-field parameters known at this time from data transformations provides a better clue to chemistry than do the spectra themselves.

The Spin Quartets of the d^3 Configuration

Ligand-field theory applies to systems for which the characterization d^q (or p^q or f^q) is more than just a consequence of a formal oxidation state.[13] Actually, one may express this fact the other way round by saying that the effective d^q configuration is responsible for the ground-state symmetry of the system and often also for that of several of the lower excited states and thereby this effective d^q configuration defines the oxidation states in a far deeper way than just a formal one. Similarly, in these cases, ligand-field theory has, in spite of its simplistic character, provided qualitative knowledge: symmetry knowledge about eigenstates, which will survive much more sophisticated theoretical treatments. Moreover, by its simplicity, the ligand-field treatment has gained a generality within inorganic chemistry which has made it live on into this age of computational chemistry.

The system that we are concerned with here is $[Cr(NH_3)_4F_2]^+$, which is—as a chromium(III) complex—a d^3 system. Moreover, as an "octahedral" d^3 complex, its ground state is $^4A_{2g}(O_h)$, or just using the rotation group, it is $^4A_2(O)$. Moreover, it is a consequence of ligand-field theory that it has the excited states $^4T_2$, a$^4T_1$, and b$^4T_1$ (in order of increasing energy) plus a number of states with a lower spin multiplicity that we shall not be concerned with here. Actually, these excited states are all observed in the aqueous solution spectrum of the complex. The special thing about this particular complex is, however, that the deviation from octahedral symmetry shows up as a splitting of all the spin-allowed transitions. This fact makes its spectrum especially valuable for analysis. It is customary to use the cubic strong-field basis to set up the energy matrices.[12] This description obtains a particularly simple form with the parametrization of eq 6. By using the ground state as the zero point of energy for the d^3 system states, one may collect together all of the ligand-field information about the spin quartets of the tetragonal system by using the cubic strong-field basis and writing

$$|3\rangle = |t_2e^2\ b^4T_1(O)\ c^4E(D_4)\ ^4A(D_2)\rangle: \quad 3B + 2\Delta(d) - {}^1/_3\Delta(t_2) \tag{18a}$$

$$|2\rangle = |t_2{}^2e\ a^4T_1(O)\ b^4E(D_4)\ ^4A(D_2)\rangle: \quad 12B + \Delta(d) + {}^1/_4\Delta(e) + {}^1/_3\Delta(t_2) \tag{18b}$$

$$|1\rangle = |t_2{}^2e\ ^4T_2(O)\ a^4E(D_4)\ ^4A(D_2)\rangle: \quad \Delta(d) - {}^1/_4\Delta(e) + {}^1/_3\Delta(t_2) \tag{18c}$$

supplemented with the nondiagonal elements

$$\langle 1|\hat{Q}[\Delta(e)]|2\rangle = ({}^3/_{16})^{1/2} = 0.4330 \tag{19a}$$

$$\langle 2|\hat{Q}[B]|3\rangle = 6 \tag{19b}$$

where the orthoaxial hierarchy specified above has been used to label the cubic strong-field states and where the nonsymmetry labels a, b, and c have been used to distinguish states with the same orbital symmetry empirically according to increasing energy. This latter labeling will survive the transition to more practical situations of intermediate cubic or tetragonal fields involving parameter values that render the total energy matrix diagonal (cf. eqs 21 and 24). By using the barycentration of the tetragonal parametric operators, one can immediately write the diagonal energy expressions for the rest of the spin quartet states that are the associated tetragonal split components, $^4A_2(D_4)$ and $^4B_2(D_4)$ of $^4T_1$ and $^4T_2$, respectively. Thus we obtain, for example, for the component associated with a$^4T_1$ b$^4E(D_4)$

$$|t_2{}^2e\ a^4T_1(O)\ a^4A_2(D_4)\rangle: \quad 12B + \Delta(d) - {}^1/_2\Delta(e) - {}^2/_3\Delta(t_2) \tag{20}$$

where the coefficients of eq 18 for the parameters representing the tetragonal field have been multiplied by −2 in order to obtain the barycentration of this orbitally nondegenerate state and its associated doubly degenerate state of eq 18. a$^4A_2(D_4)$ and b$^4A_2(D_4)$ are connected by $\hat{Q}[B]$ with the matrix element 6 as are their associated $^4E(D_4)$ states (cf. eq 19b).

It should be noted that in the same sense as the d orbitals are used to calculate the coefficients of the empirical parameters of the one-electron model, the ground state of d^3, $^4A_2(O)$, and the first excited quartet state, $^4T_2(O)$, are pure ^4F states whereas the $^4T_1$ states only are eigenstates of the orbital angular momentum when the field-strength parameter $\Sigma = \Delta/B$ of Tanabe and Sugano[14] is equal to zero. For the intermediate fields that we are concerned with here, the ^4P and ^4F terms are about 50% mixed and actually the lower $^4T_1$, a$^4T_1$, often contains slightly more than 50% of ^4P. In the strong-field basis the lower $^4T_1$, $t_2{}^2e^4T_1$, contains 80% ^4P in spite of the fact that ^4P has a higher energy than ^4F in gaseous d^3 ions.[7c]

It is convenient to discuss our results by giving them in a representation similar to that of eq 18, but different in that we use the eigenbasis of our experiment, which, of course, is the one that is diagonal as far as the sum of all the parametric terms is concerned. The results valid for atmospheric pressure (that is, 0 kbar applied pressure) are

$$|a^4A_2(D_4)\rangle: \quad 5.4660B + 1.19635\Delta(d) - 0.4018\Delta(e) - 0.4049\Delta(t_2) \tag{21a}$$

$$|b^4E(D_4)\rangle: \quad 8.5854B + 1.05403\Delta(d) + 0.1073\Delta(e) + 0.2973\Delta(t_2) \tag{21b}$$

$$|^4B_2(D_4)\rangle: \quad 0B + \Delta(d) + {}^1/_2\Delta(e) - {}^2/_3\Delta(t_2) \tag{21c}$$

$$|a^4E(D_4)\rangle: \quad 0.1984B + 1.00061\Delta(d) - 0.1191\Delta(e) + 0.3329\Delta(t_2) \tag{21d}$$

Here one obtains the transition energies by inserting the parameter values of eq 12 into eq 21. In other words, the energies of eq 21 are eigenenergies measured relative to that of the ground state, which has the symmetry characterization $t_2{}^3$

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[13] (a) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer: Berlin, 1969. (b) Bendix, J.; Brorson, M.; Schäffer, C. E. In *ACS Symposium Series 565*; Kauffman, G. B., Ed.; American Chemical Society: Washington, DC, 1994; Chapter 18, pp 213−225.

[14] Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753−766.

$^4F\ ^4A_2(O)\ ^4B_1(D_4)$. Because this state contains a half-full cubic subconfiguration, its energy expression's coefficients of the tetragonal field parameters are zero.

The second excited quartet state remains $t_2^2e\ ^4F\ ^4T_2\ ^4B_2(D_4)$ throughout for the kind of complexes belonging to the orthoaxial hierarchy of groups. Therefore, it keeps its coefficients of all the parameters constantly equal to those of eq 18.

The other excited states are easy to characterize directly on the basis of their coefficients in eq 21. The coefficients of B are measures of the contents of ^4P (energy $15B$) and ^4F (energy $0B$), coefficients of $^{15}/_2$ corresponding to 50% mixing. We conclude that the first quartet excited state $|a^4E(D_4)\rangle$ has acquired a little ^4P character by having been mixed with $^4P\ ^4T_1\ ^4E$ by the tetragonal part of the ligand field. Moreover, the combined cubic and tetragonal fields have made the third excited state $|b^4E(D_4)\rangle$ acquire more than 50% P character whereas the fourth excited state $|a^4A_2(D_4)\rangle$ has not yet reached this limit. The values of the coefficients of B compared with those of eq 18 show that the cubic strong-field limit is not very useful for quantitative parametric discussions of chromium(III) complexes. Whereas the difference between the expectation energies $\langle 2|\hat{Q}[B]|2\rangle - \langle 1|\hat{Q}[B]|1\rangle = 12$ (eq 18) in the strong-field approximation, it is $(5.466 + 2 \times 8.5854 - 2 \times 0.1984)/3 = 7.41$ for the eigenbasis of $[Cr(NH_3)_4F_2]AsF_6$ at 0 kbar.

The coefficients of $\Delta(d)$ tell about cubic subconfigurations, for example that the fourth excited state contains 19.6% t_2e^2 character.

Experimental Procedure

The high-pressure optical absorption techniques have been described elsewhere.[15] A Merrill−Bassett type diamond anvil cell (DAC) was utilized with the pressure measured by the ruby fluorescence technique. The pressure-transmitting fluid was light mineral oil. The light source was a 150 W xenon lamp with a $^1/_4$ m monochromator. Quartz light pipes were utilized between the monochromator outlet slit and the DAC and from the DAC to the photomultiplier. The data were accumulated by a photon-counting system and were collected by a computer on line.

The samples studied were synthesized by Jørgen Glerup at the University of Copenhagen. A microanalysis of the $[Cr(NH_3)_4F_2]AsF_6$ complex gave a composition essentially identical with that calculated from the formula.

Data Treatment before Ligand-field Theoretical Analysis. Since our theoretical model is essentially limited to concern transition energies represented by the peak positions of the tetragonal split components of the two lowest-energy, spin-allowed intra-d^3 transitions assigned in cubic symmetry, our primary problem is to obtain numbers that represent these peak positions. This is an extremely tricky problem in cases where the peaks do not appear to the eye as isolated maxima on the absorption curve. On the other hand, when the peaks are directly observable, the overlapping of absorption bands is a much smaller problem that can be solved satisfactorily by using curve analysis procedures. This situation makes our present chemical sample particularly valuable. Complexes containing chromophores of the type $CrN_4F_2^+$ are in fact practically the only known tetragonal complexes[9] for which the two cubically assigned bands both exhibit clearly separated split components (Figure 1).

It has been known since the 1930s that chromium(III) complexes have absorption bands that can be approximately represented by Gaussians with wavelength as the variable. The examples then were mixed complexes with ethylenediamine and oxalate.[16] Later, C.E.S. showed by analyzing a large data set that wavelength Gaussians apply well to a large number of cubic or nearly cubic complexes of chromium(III), in particular in the region between 40% and 90% of their maxima. This is not in disagreement with Jørgensen's analyses,[17] for which he used wavenumber Gaussians, which seemed physically more reasonable but which had the empirical disadvantage of requiring two different half-widths on the high-energy and low-energy sides, which caused them also to have two different curvatures at their maxima. Jørgensen did not use his Gaussians for curve analyses, but rather for estimation of intensities. For our present purposes the wavenumber Gaussians have the disadvantage of having two many parameters (an extra half-width). We therefore analyzed our data using wavelength Gaussians and found them satisfactory. In order to perform the analysis, we eliminated for each spectrum all data corresponding to energies below ca. 1.6 μm^{-1} and above ca. 3.4 μm^{-1} plus a single data point at 1.734 μm^{-1}, which invariably singled itself out and which was assigned as a narrow component of one of the spin-forbidden transitions.

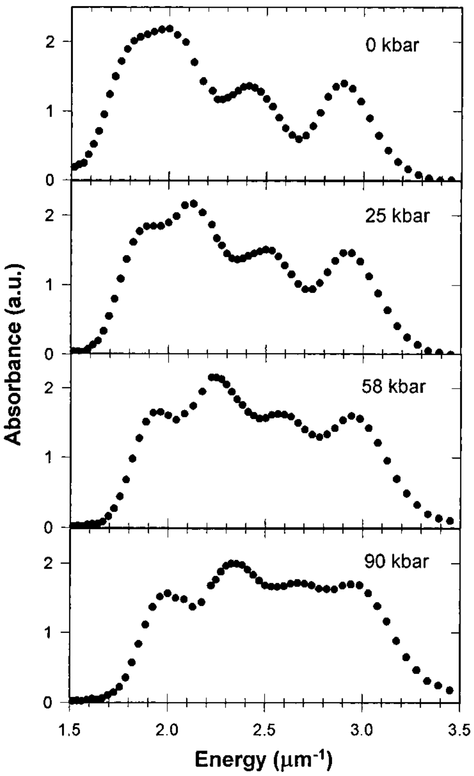

Figure 1. Spectra of *trans*-$[Cr(NH_3)_4F_2]AsF_6$ at various pressures.

In the curve fitting analyses, the maximal absorption peak was normalized to unit absorbance. We then obtained variances of about 3×10^{-5} for the wavelength Gaussians using 45 data points of unit weight. This corresponds to a standard deviation of 0.0008 absorbance units, which is an unrealistically good fit (~0.1% at the maxima), caused by the fact that the four Gaussians with $12 - 1 = 11$ independent parameters provide a body-stocking adaptation to an absorption curve of the type of Figure 1, which does not contain enough information to determine the 12 parameters very well. Nevertheless, a model using four symmetrical wavenumber Gaussians gave standard deviations that were about 10 times higher.

The important point is that the changes in peak location and splitting are very large compared with the scatter of the points shown in Figure 2 so that we can draw firm conclusions.

Pressure Tuning of the Ligand-Field Spectra of $[Cr(NH_3)_4F_2]AsF_6$

Figure 1 shows typical spectra of $[Cr(NH_3)_4F_2]AsF_6$. Figure 2 shows the peak positions of the first four spin-allowed transitions of $[Cr(NH_3)_4F_2]AsF_6$ with increasing pressure, assigned in tetragonal symmetry (cf. eqs 18, 20, 21, and 24). The first two peaks are those which approximately have the first excited state $^4T_2$, assigned in octahedral symmetry, as its parentage, and the next two similarly correspond to a^4T_1. The assignments were made as in the past on the basis of chemical induction[9] as well as single-crystal polarized spectral analysis.[18]

It is a reassuring experience to have semiquantitative visual perception of all four peaks' increase with pressure by a

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(15) Lang, J. M.; Drickamer, H. G. *J. Phys. Chem.* **1993**, *97*, 5058−5064.

(16) Mead, A. *Trans. Faraday Soc.* **1934**, *30*, 1052−1058.

(17) Jørgensen, C. K. *Acta Chem. Scand.* **1954**, *8*, 1495−1501.

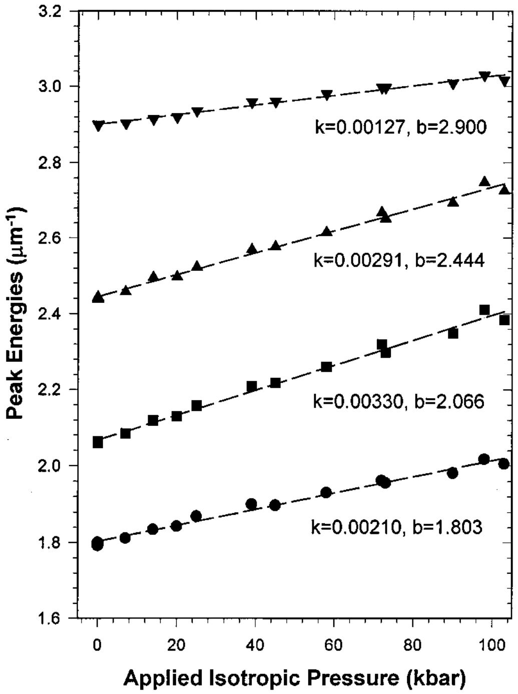

Figure 2. Peak shift vs pressure: four fitted peaks for *trans*-[Cr(NH$_3$)$_4$F$_2$]AsF$_6$. Slopes (*k*) and intercepts (*b*) of linearizations are given.

comparison of the four direct data sets of Figure 1, which also reveal that the splitting of the first “cubic” band increases whereas that of the second “cubic” band decreases. This increase of the first band splitting concomitant with the increasing energy of both of its components is an indication that Δ_N and Δ_F both increase with pressure, but Δ_N more so than Δ_F. Figure 2 quantifies the visual perceptions and shows that the peak positions increase linearly with pressure within the uncertainty of the (slightly transformed) data. This figure includes all of our 13 data sets.

We measured [Cr(en)$_2$F$_2$]I and obtained qualitatively the same results as those just discussed for [Cr(NH$_3$)$_4$F$_2$]AsF$_6$. However, the excited state a^{4}T$_1$a^{4}A$_2$ is situated not far from the region of rising absorption toward the UV, thereby rendering the quantitative estimates of the peak positions uncertain.

Figure 3 shows the results of the data transformation in terms of the variation of the orbital energies with pressure. In the calculation of these orbital energies the linear functions given in Figure 2 were used. Since the transformation is not quite linear, a smooth curve between the sets of points of Figure 3 is not a straight line. The full-line curves drawn represent the cubic average energies of the orbital sets e(*O*) and t$_2$(*O*). These energies are immediately defined as weighted averages for these complexes because the four orbital sets do not have any symmetry species of D_4 in common and therefore cannot be mixed by the tetragonal field. At atmospheric pressure, the complex shows σ- as well as π-compressed orbital-energy tetragonality, Δ(e) and Δ(t$_2$) both being negative. Both tetragonal splitting parameters increase with pressure, and their absolute values decrease accordingly. The variation of Δ(e) makes the complex change from being tetragonally σ compressed to becoming σ elongated at approximately 85 kbar. At this pressure, the complex is cubic as far as the σ interactions are concerned.

Δ(d) increases by about 12% between 0 and 100 kbar of applied pressure. If we assume an average variation with distance that follows an r^{-6} law,[11] this means that the 100 kbar pressure has resulted in a 2% decrease in average metal to ligand bond distance. Even though the stress that we applied is isotropic, the strain is not, at least not when the anisotropy is estimated on the basis of ligand-field parameters. We shall now discuss this aspect.

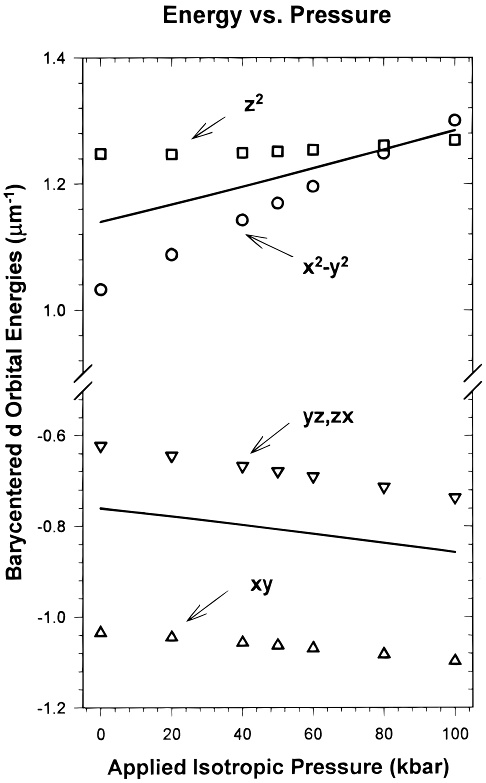

Figure 3. Variation of orbital energies with pressure calculated from the straight lines of Figure 2. The solid lines represent the average energies of the e(*O*) and t$_2$(*O*) sets of orbitals.

Referring to our results at 0 kbar, already discussed in connection with eqs 12 and 13, we now provide our results at 100 kbar

$$\Delta = 2.141, \quad \Delta(\mathrm{e}) = +0.0303,$$
$$\Delta(\mathrm{t}_2) = -0.3600 \qquad (\text{all in } \mu\mathrm{m}^{-1}) \tag{22}$$

$$\Delta^2\langle\hat{Q}[\Delta]|\hat{Q}[\Delta]\rangle = 5.50\,\mu\mathrm{m}^{-2} \tag{23a}$$

$$[\Delta(\mathrm{e})]^2\langle\hat{Q}[\Delta(\mathrm{e})]|\hat{Q}[\Delta(\mathrm{e})]\rangle = 0.0005\,\mu\mathrm{m}^{-2} \tag{23b}$$

$$[\Delta(\mathrm{t}_2)]^2\langle\hat{Q}[\Delta(\mathrm{t}_2)]|\hat{Q}[\Delta(\mathrm{t}_2)]\rangle = 0.0866\,\mu\mathrm{m}^{-2} \tag{23c}$$

and observe that the cubic field now amounts to as much as 98.4% and the combined tetragonal fields 1.6%. This is a halving of the tetragonal fields’ contribution to the sum-square splitting. So the isotropic stress results in a more isotropic complex ion. This result could not have been obtained from the raw spectra. Here the data transformation into one-electron energies as well as the sum-square-splitting analysis was essential.

The Racah parameter *B* decreases rather smoothly from 0.0694 μm^{-1} at 0 kbar to 0.0658 μm^{-1} at 100 kbar. This is in agreement with previous findings for octahedral complexes,[11] but these were not particularly clear-cut. It is therefore gratifying that the present homogeneous data set confirms this increase in nephelauxetism[3] with pressure, which is the expected

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(18) Dubicki, L.; Hitchman, M. A.; Day, P. *Inorg. Chem.* **1970**, *9*, 188–190.

variation if the usual interpretation of nephelauxetism as being a consequence of increasing covalency is to be accepted.

The parametric expressions for the energies of the excited states at 100 kbar are given in eq 24. When the parametric

$$a^4A_2(D_4)\rangle:\quad 7.6043B + 1.09587\Delta(\mathrm{d}) - 0.4521\Delta(\mathrm{e}) - 0.5388\Delta(\mathrm{t}_2) \tag{24a}$$

$$b^4E(D_4)\rangle:\quad 9.1795B + 1.04288\Delta(\mathrm{d}) + 0.2545\Delta(\mathrm{e}) + 0.3047\Delta(\mathrm{t}_2) \tag{24b}$$

$$^4B_2(D_4)\rangle:\quad 0B + \Delta(\mathrm{d}) + {}^1/_2\Delta(\mathrm{e}) - {}^2/_3\Delta(\mathrm{t}_2) \tag{24c}$$

$$a^4E(D_4)\rangle:\quad 0.0033B + 1.00001\Delta(\mathrm{d}) - 0.2654\Delta(\mathrm{e}) + 0.3333\Delta(\mathrm{t}_2) \tag{24d}$$

values of eq 22 are inserted into eq 24, the transition energies at 100 kbar are obtained. The combined effect of the increased value for Δ(d) and the decreased value of *B* results in much more cubic strong-field-like energy expressions in eq 24 than in eq 21. This can be clearly seen by comparing these two equations with eq 18. In terms of the field strength $\Sigma = \Delta/B$, this parameter ranges from 27.4 (0 kbar) to 32.5 (100 kbar).

Pressure Dependence of Single-Ligand Parameters

In eqs 14 and 16 the three parameters of the holistic model are related to the four single-ligand parameters of the AOM. The information contained in our experiment allows only three independent orbital energy parameters to be determined. Therefore, some sort of reduction of the number of single-ligand parameters is necessary and it was chosen to use the π parameter $\Delta_{\pi N}$ referring to NH_3 as the zero point of energy for the other parameters. This choice was thought to be a fortunate one in view of the interpretation of the parameters as being parametric expressions of the donor properties of the ligands toward the central ion d orbitals. The fact that NH_3 has no π lone pairs should then secure that the parameter $\Delta_{\pi N}$ was zero or at least small compared with the other parameters of Δ_π type. This information is a prerequisite for the following discussion. It should also be remembered that the theoretical part of the AOM is the coefficients of its energy parameters while its parameters must be thought of as expressions of a data reduction, made possible by the model.

Upon insertion of the holistic parametric results of eq 22 into eq 16, the following single-ligand parameters, valid at 100 kbar, emerge:

$$\Delta_N = 2.396,\quad \Delta_F = 1.631,\quad \Delta_{\sigma F} = 2.351,\quad \Delta_{\pi F} = 0.721 \quad (\text{all in } \mu\mathrm{m}^{-1}) \tag{25}$$

These results should be compared with those of eq 17, which are valid at 0 kbar. The two values Δ_N and Δ_F exhibit increases of 16% and 4%, respectively. $\Delta_{\sigma F}$ and $\Delta_{\pi F}$ decrease by 2% and 12%, respectively. The results for the two Δ values are just what should be qualitatively expected in view of previous experience from pressure-tuned spectra of octahedral complexes. The general question that we were asking here was, however, how the pressure increase of Δ_J applying to a specific ligand J was distributed upon its two parts $\Delta_{\sigma F}$ and $\Delta_{\pi J}$. We now have the answer as far as the parameters referring to fluoride are concerned, provided we can assume that $\Delta_{\pi N}$ is zero at all pressures. This is the parametric answer from the model we have used, together with the data transformation of our experiments we have made, namely that the difference quantity Δ_F increases with pressure while its two components according to eq 15 decrease in such a way that the most rapidly decreasing component is that having a negative coefficient (cf. eq 15). We cannot, of course, exclude that these decreases fully or partially are caused by increases of $\Delta_{\pi N}$ with pressure.

Table 1. Energy Parameter Derivatives with Respect to Pressure in Units of μm^{-1} $kbar^{-1}$

	dΔ/d*p*	dΔ(e)/d*p*	dΔ(t_2)/d*p*	d*B*/d*p*
0 kbar	0.0022	0.0029	0.0006	0.000005
100 kbar	0.0025	0.0021	0.0004	−0.00004
averages, 0−100 kbar	0.0024	0.0025	0.0005	−0.00003

In the comparison of eqs 17 and 25, it is not easy to discern the increasing isotropy with pressure which we inferred in the preceding section on the basis of the sum-square-splitting results. The reason for this is that the three independent single-ligand parameters do not belong to mutually orthogonal coefficient operators. The very concrete consequence of this is that if the one-electron energies of eq 6 are written in terms of the single-ligand parameters of eq 16 and the s.sq.s. is calculated, then part of the s.sq.s. occurs in cross products of the parameter values. Thus the s.sq.s. cannot be simply analyzed by using the single-ligand parameters.

From eq 14 together with eqs 17 and 25, it appears, however, that the σ difference parameter, Δ(e), and the π difference parameter, $\Delta(t_2)$, show a decrease in their absolute values with pressure; and both of these are members of a set of mutually orthogonal operators.

Consequences of the Nonlinearity of the Data Transformations

In obtaining the orbital energy parameters given in eqs 12 and 22, we used our full set of data for Figure 3 by assuming that the pressure dependence of the peaks was actually linear. Since the data transformation is nonlinear, this assumption has the consequence that neither the orbital energy parameters of eq 14a nor the one-electron energies will vary linearly with pressure. By using the constant slopes of the curves of Figure 2, it is possible to find the limiting slopes of the three orbital energy parameters and of the Racah parameter *B* from eqs 21 (0 kbar) and 24 (100 kbar). The results are given in Table 1 together with the average slope over the entire pressure region. The discrepancy is clearly minor and possibly not even discernible within the accuracy of the data treatment. It maximizes for Δ(e), which at 50 kbar takes the value −0.092 μm^{-1} when linearly interpolated from Δ(e) versus *p* whereas its value calculated from the linear functions of the observed peaks is −0.082.

Conclusion

The effect of pressure on the ligand-field spectrum of the salt $[Cr(NH_3)_4F_2]AsF_6$ has been measured up to 100 kbar. The spin-allowed cubic bands both split in the tetragonal symmetry of the molecular ion and the peaks all blue-shift linearly with pressure (Figures 1 and 2).

From these linear relations, the pressure dependencies of the one-electron energies and of the Racah parameter *B* have been calculated by using the holistic ligand-field model, which is essentially based upon symmetry.

The fact that our one-electron operators are mutually orthogonal allows us to express the sum-square splitting (s.sq.s.) of our one-electron energies as a sum of contributions from each of our three one-electron parameters. The result of this quantification (eqs 13 and 22) is that the s.sq.s. increases by

25% from 0 to 100 kbar and that the ligand field becomes much more isotropic (cubic) with increasing pressure.

The results may be interpreted by using the angular overlap model. There is an analogy between the two half π bonds in the oxygen molecule and those in the F−Cr−F system. In both cases, the antibonding component orbitals of the interaction are only half full of electrons. The partial double-bond character of the chromium(III)−fluoride bonds, resulting from the additional formation of a coordinate bond from the filled fluoride π orbitals to the half-filled d_{zx} and d_{yz} orbitals, as evidenced by the large σ and π AOM parameters for the Cr−F bond, makes these bonds less compressible than the chromium(III)−nitrogen single bonds. During the compression, the chromium−nitrogen σ parameter $\Delta'_{\sigma N}$ increases so much as to become larger than the corresponding chromium−fluoride parameter $\Delta'_{\sigma F}$. This σ parameter as well as the π parameter $\Delta'_{\pi F}$ decreases slightly with pressure, possibly an indication of the resistance of the system against charge accumulation (the donor parameter of nitrogen increases; accordingly those of fluoride decrease). It would have been nice to see the bond-length picture of these pressure events, but that lies in the future.

One obtains a chemical perspective of the size of the pressure effects by noting the comparison of the data set (Δ, B)/μm^{-1} for $Cr(NH_3)_6^{3+}$, (2.16, 0.0651),[19] with that for the 100 kbar spectrum of $[Cr(NH_3)_4F_2]AsF_6$, (2.14, 0.0658). The two data sets are close.

Since the model that we have been using throughout contains the two essentially different terms, repulsion and ligand field, it would as a final issue be interesting to address the question as to how much these two contributions mean in comparison with each other. This question finds a quantitative answer by noting that their operators are mutually orthogonal. If we consider the sum-square splitting of the 10 quartet states with $M_S = {}^3/_2$ for which the norm square of the barycentered $\hat{Q}[B]$ is found to be 256.5 and the one-electron operator norm squares are found to take values 3 times those given in eqs 10 and 11, then we obtain the results that repulsion makes up $0.0694^2 \times 256.5/(0.0694^2 \times 256.5 + 1.9^2 \times 3.6 + 0.215^2 \times 1.5 + 0.412^2 \times 2) = 8.4\%$ at 0 kbar (eq 12) and 6.2% at 100 kbar (eq 22) of the sum-square splitting. Even though the cubic strong-field approximation is a poor approximation of the eigenstates, as we realized in connection with eq 24, it is still the one-electron energies that dominate the issue as far as the splitting of the spin quartets of the d^3 configuration is concerned.

Acknowledgment. We are indebted to two people from the University of Copenhagen: Jørgen Glerup for the sample of $[Cr(NH_3)_4F_2]AsF_6$ and Jesper Bendix for the program LIGFIELD which was of indispensable help to us in doing the parametric analyses of the data.

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[19] Schäffer, C. E. *J. Inorg. Nucl. Chem.* **1958**, *8*, 149−154.