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# Polynuclear Chromium(III) Complexes with Bromide Bridging. Thermal and Magnetic Studies

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## Abstract

Two new polynuclear chromium(III) complexes with a bromide bridge have been prepared and characterized. One of them is a dinuclear with two $Br^-$ as a bridging ligand; the other is presumably an angular trinuclear with only one $Br^-$ as a bridging ligand between each pair of Cr(III) ions. The complexes were prepared by heating in the solid state the known precursor complexes $[CrF_2(aa)(H_2O)_2]Br$ (aa = ethylenediamine or 1,2-cyclohexanediamine). By means of TG measurements the kinetic parameters have been calculated for the two processes. The activation energy, $E_a$, is very low in both cases indicating a dissociative mechanism and an open structure in the crystal lattice. The magnetic measurements up to helium liquid temperature indicate a weak antiferromagnetic coupling constant in the trinuclear complex of ethylenediamine but a Curie law behaviour in the dinuclear compound of 1,2-cyclohexanediamine.

## Introduction

The two complexes $[CrF_2(aa)(H_2O)_2]Br$, aa = ethylenediamine(en) or 1,2-cyclohexanediamine(chxn), have been described in the literature [1]. By heating of the en complex, the new complex $[CrBrF_2(en)(H_2O)]$ is obtained, according to the same literature. Our experience with this complex and with the analogous $[CrF_2(chxn)(H_2O)_2]Br$ allows us to suggest that the heating of the chxn complex at controlled temperature, produces the dinuclear $[(chxn)F_2Cr{-}(Br)_2{-}CrF_2(chxn)]$ complex before the total decomposition. Instead, in the en complex, the two molecules of coordination water are lost simultaneously or, at least, it is impossible to separate them in the TG diagrams. Moreover, the dinuclear complex with a di-$\mu$-Br bridge cannot be attained before the decomposition, but a trinuclear one, of unknown structure, in which the Cr(III) atoms are linked together with one Br bridge atom, is obtained.

The different behaviour of the two complexes cannot be explained at the present time. The formation of the dinuclear species is very similar to that described in the literature for the series $[Cr(OH)(aa)_2(H_2O)]S_2O_6$ which by prolonged heating give the dinuclears $[(aa)_2Cr{-}(OH)_2{-}Cr(aa)_2](S_2O_6)_2$ [2]. The formation of a trinuclear is more surprising as there is nothing corresponding to it in the literature on solid state reactions of the complexes of chromium(III). All the experimental facts (TG and magnetic measurements up to the helium liquid temperature) support this hypothesis.

## Experimental

### *Synthesis*

The two complexes $[CrF_2(aa)(H_2O)_2]Br$ (aa = chxn, en) were prepared as previously reported [1].

### *Techniques*

Electronic absorption spectra were recorded in the solid phase (KBr disk or diffuse reflectance) on a Beckman 5230 UV spectrophotometer. Thermal analysis was carried out on a Perkin-Elmer Model TGS-2 system, under a nitrogen atmosphere (10 $cm^3$ $min^{-1}$), the sample size being in the range 4–7 mg. The heating rate for non-isothermal experiments was 5 °C $min^{-1}$. Kinetic calculations were made on the basis of the thermogravimetric analysis both in non-isothermal and isothermal conditions. We have used all the principal expressions of $g(\alpha)$ ($\alpha$ being the fraction decomposed) given in the literature (Table I). Magnetic measurements were made with a Faraday-type magnetometer, equipped with a helium flow cryostat. Measurements were performed in the 4.2–300 K range. The calculations for TG and magnetic measurements were made with an *ad hoc* FORTRAN IV program.

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TABLE I. Kinetic functions, $g(\alpha)$, Used in their Integral Form ($\alpha$ = mole fraction decomposed)

| Mechanism | g(α) | |
|---|---|---|
| Nucleation controlled | | |
| Power law | $\alpha^{1/n}$ | $R_1$ |
| Growth controlled | $[1-(1-\alpha)^{1-n}]/(1-n)$ | $R_2$, $R_3$ |
| for $n = 1$ | $[-\ln(1-\alpha)]$ | $F_1$ |
| Nucleation–Growth controlled | | |
| Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/n}$ | $A_2$, $A_3$ |
| Diffusion controlled | | |
| One-dimensional | $\alpha^2$ | $D_1$ |
| Two-dimensional | $\alpha + (1-\alpha)\ln(1-\alpha)$ | $D_2$ |
| Three-dimensional | $[1-(1-\alpha)^{1/3}]^2$ | $D_3$ |
| Three-dimensional | $(1-2/3\alpha)-(1-\alpha)^{2/3}$ | $D_4$ |

## Results and Discussion

### *Complexes Obtained by Heaing of* $[CrF_2(aa)(H_2O)_2]Br\cdot nH_2O$

The dynamic TG run is different for aa = en or chxn (Fig. 1). When the amine aa is 1,2-cyclohexanediamine (chxn) the TG curve presents two losses of water: the first step corresponds exactly to 2.5 molecules of water and the second step corresponds to the loss of only one molecule of water. Taking into account the formula proposed, $[CrF_2(H_2O)_2(chxn)]Br\cdot 1.5H_2O$, the first step must correspond to the loss of all the water of crystallization (1.5 moles) and 1 mole of coordinated water, the second step must correspond to the loss of the second molecule of coordinated water. This experiment indicates the fact frequently observed in complexes with two kind of water (crystallization and coordination) the crystallization water helps the loss of coordination water at a lower temperature. For this reason, in the present complex, the two coordination water molecules can be separated. In the first step only one coordination water molecule is lost (together with the 1.5 molecules of crystallization water).

At a low temperature (Table II) the heated complex still presents one molecule of water, giving the complex of formula $[CrF_2Br(chxn)(H_2O)]$; at high temperature, this molecule of water is lost, giving a dinuclear complex whose formula may be $[(chxn)F_2Cr{-}(Br)_2{-}CrF_2(chxn)]$. The temperature intervals are given in Table II.

When aa = ethylenediamine a single loss of water is observed, corresponding to 5 moles of water for 3 moles of starting complex. The temperature at which the reaction begins is very high (*ca.* 145 °C) (Table II), clearly indicating the anhydrous character of the complex, already determined by chemical analysis. Evidently in the hypothetical case of the loss of all the water molecules, it should be 6 moles of water for 3 moles of complex (1:2). But all the TG experiments indicate that the water molecules lost are only five. After the loss of these 5 molecules of water, there is a total and continuous decomposition.

The new complex can correspond to a trimer of chromium(III), according to the following reaction:

$$3[CrF_2(en)(H_2O)_2]Br \longrightarrow [(H_2O)(en)F_2Cr{-}Br{-}CrF_2(en){-}Br{-}CrF_2Br(en)] + 5H_2O$$

The final products have been characterized by chemical analysis (compared with the formula proposed), IR and electronic spectra and magnetic measurements up to the helium liquid temperature. The analysis of the trinuclear complex, when not freshly prepared, indicated two molecules of water per formula proposed. This fact could be due to the hygroscopic character of the new trinuclear. This new water molecule can be either water of crystallization or coordination water due to the weak character of the Cr–Br(terminal) bond. The Br ending ligand can be substituted by $H_2O$ giving an ionic compound of formula $[(H_2O)(en)F_2Cr{-}Br{-}CrF_2(en){-}Br{-}CrF_2(en)(H_2O)]Br$.

The IR spectra were not very indicative of the changes in the coordination. Only the bands due to the water (3000 cm$^{-1}$ region) were different, indicating the anhydrous character or not of the studied complexes.

Taking into account that the two new complexes undergo rapid aquation in solution, the electronic spectra were recorded in the solid state. In Table III the maxima of the absorption are given together

TABLE II. Interval Temperatures and % Water Loss for the Anation Reactions

| Reaction | $T_i$ (°C) | $T_f$ (°C) | %$H_2O$ | |
|---|---|---|---|---|
| | | | calc | found |
| $[CrF_2(chxn)(H_2O)_2]Br\cdot 1\frac{1}{2}H_2O \longrightarrow [CrF_2Br(chxn)(H_2O)]$ | 25 | 115 | 12.97 | 12.7 |
| $2[CrF_2Br(chxn)(H_2O)] \longrightarrow 2H_2O + [(chxn)F_2Cr{-}(Br)_2{-}CrF_2(chxn)]$ | 115 | 140 | 5.96 | 5.9 |
| $3[CrF_2(en)(H_2O)_2]Br \longrightarrow$ trinuclear + $5H_2O$ (see text) | 145 | 205 | 11.17 | 11.1 |

TABLE III. Electronic Absorption Spectra of the New and Parent Complexes in the Solid State

| Complex | $\lambda_{max}$ (nm) | | | |
|---|---|---|---|---|
| $[CrF_2(en)(H_2O)]Br$ | 544 | 415(sh) | | 372 |
| Trinuclear of en (see text) | 560 | | 400 | |
| $[CrF_2(chxn)(H_2O)_2]Br$ | 546 | 415(sh) | | 375 |
| Dinuclear of chxn (see text) | 570 | | 400 | |

with those of the precursor species. We can observe that the first maximum is displaced *ca.* 25 nm towards higher wavelengths due to the substitution of the water by bromide in the coordination sphere of Cr(III). In the trinuclear complex the shift is lower than in the dinuclear one, due to the existence of two molecules of water in the trinuclear after heating.

### *TG Measurements and Kinetic Parameters Calculation*

The first condition to calculate the kinetic parameters in a solid state reaction is to have a very definite process in the TG runs. Consequently, in the chxn case, when the loss of the crystallization and coordination water occurs simultaneously, the calculation of the average $E_a$ has no sense. However, the loss of the second coordinated molecule (which corresponds to the dimer formation process) is clear and definite: $E_a$ can be easily calculated.

In the en complex, the global process is very complicated, but taking into account the anhydrous character of the complex, we can write the global process as above. Consequently, taking this process as unique, we can calculate the $E_a$ of the reaction.

In order to determine the kinetic parameters we have registered one non-isothermal TG run for the two studied substances. The temperature interval for the dehydration–anation processes are given in Table II. The new species formed, characterized by analysis and spectroscopic measurements, are also indicated in Table II. From non-isothermal TG runs we selected several temperatures in the anation interval to carry out the isothermal TG curves necessary to calculate the kinetic parameters. The final products of the isothermal TG were also analyzed and studied by electronic spectroscopy.

The kinetic parameters were determined on the basis of the general kinetic relation [3]

$$g(\alpha) = \int_{t_1}^{t_2} k(T)\mathrm{d}t \qquad (1)$$

where $\alpha$ is the fraction decomposed and $k(T)$ follows the Arrhenius law, $k(T) = k_o\exp(-E_a/RT)$, with $k_o$ being the frequency factor and $E_a$ the activation energy. The expression $g(\alpha)$ depends on the mechanism of the solid state reaction (Table I): diffusion, nucleation, nucleation-growth or growth. Each process can be studied using several expressions of $g(\alpha)$ depending on $\alpha$ and $n$ (the reaction order) [3].

Kinetic parameters are impossible to calculate with precision using only non-isothermal TG curves due to the ignorance of the true $g(\alpha)$ expression [4]. Instead, with the isothermal method, the $E_a$ is almost independent of the physical method employed [5]. Consequently, we can take this $E_a$ value to be the 'true' $E_a$ of the solid state process.

Finally, the physical mechanism is assigned on the basis of agreement of the activation energy, frequency factor and $r^2$ (regression coefficient) values in both non-isothermal and isothermal methods. The final average kinetic parameters calculated are given in Table IV. The detailed method to solve eqn. (1) and to find $E_a$ by isothermal and non-isothermal methods is given in our previous reports [6, 7].

From the results of Table IV we can conclude, first of all, that $E_a$ is very low in both cases. Taking into account the Crystal Field Activation Energy (CFAE), according to the theory of Basolo and Pearson [8] for homogeneous kinetics, high values of $E_a$ have a better correspondence with an $S_N2$ mechanism while low values have a better correspondence with an $S_N1$ [8].

The mechanism, therefore, might be, in our case $S_N1$ (dissociative) with the formation of a square-base pyramid activated complex, requiring only 2.00 *Dq* (*Dq* being about 25 kJ/mol for Cr(III) (for a trigonal-bipyramid activated complex it would require 5.7 *Dq*). Consequently the transition state is determined by the loss of water and a non-ionic Frenkel defect formation.

TABLE IV. Kinetic Parameters for the Two Dehydration–Anation Reactions[a]

| | Physical model | $E_a$ (kJ/mol) | log $k_o$ | $\Delta S^{\#}$ (cal/K mol) |
|---|---|---|---|---|
| $2[CrF_2Br(chxn)(H_2O)] \rightarrow$ dinuclear + $2H_2O$ | Nucleation–Growth<br>$n = 3$ | 82.2 | 9.9 | $-22.5 \pm 5$ |
| $3[CrF_2(en)(H_2O)_2]Br \rightarrow$ trinuclear + $5H_2O$ | Nucleation–Growth<br>$n = 1.5$ | 76.4 | 9.0 | $-33.3 \pm 4$ |

[a] The values are reported for 1 mol of the starting product.

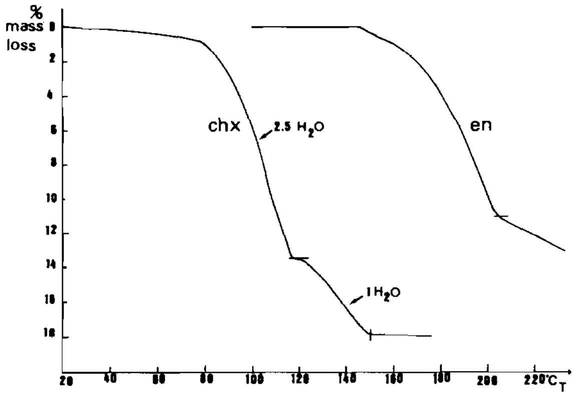

Fig. 1. Non-isothermal curve for $[CrF_2(H_2O)_2(chxn)]Br \cdot 1.5H_2O$ and $[CrF_2(H_2O)_2(en)]Br$.

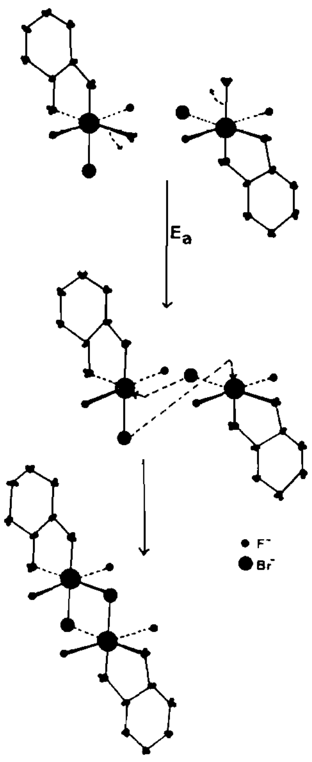

Fig. 2. Mechanism for the dehydration of $[CrF_2Br(chxn)(H_2O)]$ to give the dinuclear $[(chxn)F_2Cr(Br)_2CrF_2(chxn)]$ complex.

In the en compound it is not possible to propose a mechanism for the chemical process although we think that interaction between the pentacoordinate intermediate $[CrF_2(en)(H_2O)]^*$ and the $Br^-$ ion will be responsible for the formation of the trimer. The $E_a$ value (Table IV) is lower than those obtained with the *trans*-$[CrF(aa)_2(H_2O)]^{2+}$ complexes [7], indicating a less compact structure, according to the theory of the 'free space' elaborated by House [9] and repeatedly confirmed by us [6, 7, 10].

On the other hand, the lower $E_a$ values in the chxn complex are in accordance with the results given in our previous works with *trans*-$[CrF(chxn)_2(H_2O)]X_2$ complexes [7, 11] in which, when the temperature of the reaction is greater than 160 °C, there is a cleavage of the Cr–N(amine) bond; when the temperature of the reaction is lower than 160 °C (as in the present case), there is no cleavage of the Cr–N(amine) bond.

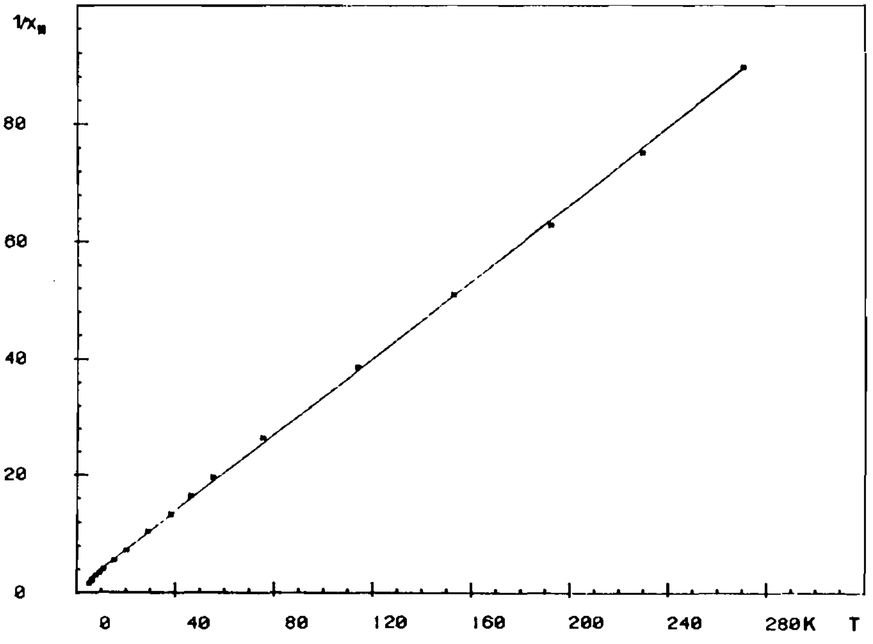

Fig. 3. $1/\chi_M$ *vs.* $T$ of $[(chxn)F_2Cr(Br)_2CrF_2(chxn)]$ complex.

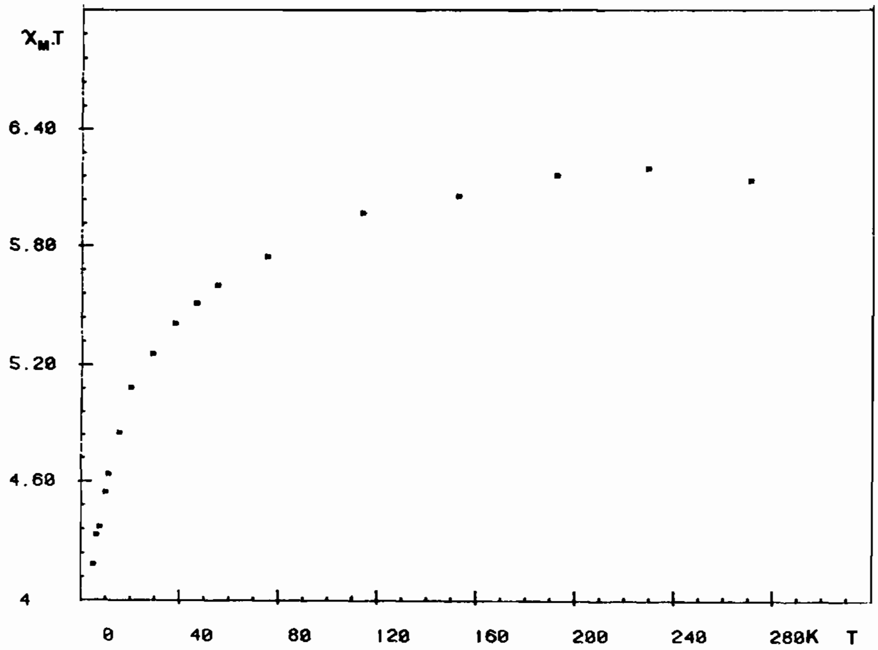

Fig. 4. $\chi_M T$ *vs.* $T$ for the en trinuclear complex.

Consequently, the mechanism of the formation of the dinuclear can be shown schematically as in Fig. 2.

First, a pentacoordinate intermediate is formed (the $E_a$ calculated corresponds to this step); secondly, there is the formation of the bonding between two pentacoordinate species, giving the dinuclear complex.

### *Magnetic Measurements*

In the literature there is a great number of polynuclear chromium(III) complexes with several bridge ligands such as $OH^-$, $O_2^-$, alcoxo, etc. [12–15] but not with the $Br^-$ ligand. In the absence of structural factors, we report here the phenomenological approach for two new polynuclear chromium(III) complexes with $Br^-$ as bridging ligand.

With regard to the dinuclear complex of chxn, in Fig. 3 is represented the inverse of the susceptibility *versus* $T$. It can be easily deduced that the new complex follows the Curie law. Consequently, there is no coupling between the two Cr(III) ions, linked by $Br^-$ bridge. Instead, the curve of $\chi T$ *versus* $T$ for the trinuclear complex is represented in Fig. 4, clearly indicating an antiferromagnetic coupling between the two Cr(III) ions.

In this case, starting from the general Van Vleck equation

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\,\frac{\Sigma S'(S'+1)(2S'+1)\exp(-E/kT)}{\Sigma(2S'+1)\exp(-E/kT)} \qquad (2)$$

where $S' = S_1 + S_2 + S_3$ ($S_1 = S_2 = S_3 = 3/2$) we can suppose a linear or an angular trinuclear. That is to say, there will be two different coupling constants, $J$ between the two coupled Cr(III) ions and $J'$ between the terminal non-coupled Cr(III) ions. In our case, we suppose that $J' = 0$. With this hypothesis, the spin Hamiltonian used is $H = -J(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3)$. The final equation for the trinuclear will be

$$\begin{aligned}\chi = (Ng^2\beta^2/4kT)\,&(165e^{21x/2} + 84e^{9x} + 35e^{15x/2}\\ &+ 94e^{6x} + 35e^{11x/2} + 10e^{5x} + 35e^{5x/2} + e^{3x/2}\\ &+ 10)/(5e^{21x/2} + 4e^{9x} + 3e^{15x/2} + 6e^{6x} + 3e^{11x/2}\\ &+ 2e^{5x} + e^{7x/2} + 2e^{3x} + 3e^{5x/2} + e^{3x/2} + 2)\end{aligned} \qquad (3)$$

with $x = J/kT$

$$\chi = f(J)(1-\rho) + 5\rho N\beta^2/kT \qquad (4)$$

The best fit of the data to eqn. (4) (which is the same as eqn. (3) with paramagnetic impurities) is found with the following parameters: $J = -3.5/-3.8$ cm$^{-1}$; $g = 2.1$ and $\rho = 0.1$–$0.15$ with $R = 0.07$–$0.1$ and $R_w = 0.07$–$0.1$; $R = \sqrt{\Sigma(\chi_{exp} - \chi_{calc})^2/\Sigma\chi_{exp}^2}$ and $R_w = \sqrt{\Sigma(\chi_{exp} - \chi_{calc})^2/\chi_{exp}/\Sigma\chi_{exp}}$.

In this case, the greater value of $\rho$ (more than 10%) cannot be taken only as 'impurities' but, rather, as a monomeric unit not yet reacted, mixed with decomposition products. We must take into account that the magnetic measurements have been made on the direct heated samples, without possibility of further purification.

The small values of $J$ indicates a small antiferromagnetic coupling between the chromium(III) ions. The expected structure for the compound is given in Fig. 5. The value of $J$ is of the same order as the value recently described for the lineal trinuclear chromium(III) complex with 1,5-diphenyl-1,3,5-pentanetrionate [15].

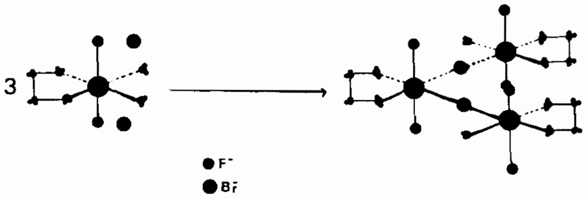

Fig. 5. Proposed structure for the trinuclear complex of ethylenediamine ligand.

On the other hand, it is surprising that in the dinuclear complex there is no antiferromagnetic coupling (or, at least, it is lower than 0.1 $\mathrm{cm}^{-1}$). This fact can be explained by supposing that the structure of the dinuclear is with a double $\mathrm{Br}^-$ bridge, instead of a single $\mathrm{Br}^-$ bridge as in the trinuclear one. Taking into consideration that $J = J_{\mathrm{antiferro}} + J_{\mathrm{ferro}}$ [16] and according with Hodgson [12] about the variation of $J$ *versus* $\varphi/R$, in our structure we can suppose that the two contributions are almost equal but with the opposite sing. Lack of knowledge of the structure prevents us from providing a complete interpretation.

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