

The Diamagnetic Susceptibility and the High-Frequency Term in Co(III)- and Rh(III)-Complexes

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A number of diamagnetic Co(III)- and Rh(III)-complexes are discussed on the basis of Van Vleck's formula for the magnetic susceptibility. It seems possible to correlate the measured magnetic susceptibility with the tendency for forming "covalent" complexes by means of a calculation of the high-frequency term in this formula. As to be expected it is found that the "degree of covalency" for different ligands follows the spectrochemical series closely. The theory gives an interpretation of the variation of the magnetic susceptibilities in the series of complex ions $\text{Co}(\text{NO}_2)_n(\text{NH}_3)_{6-n}$.

In this note the measured magnetic susceptibilities of various diamagnetic Co(III)- and Rh(III)-complexes will briefly be considered for the purpose of studying the bonding in these compounds. Diamagnetism of a complex has in the past generally been taken as an indication of "covalency" if spin magnetism could be attributed to the gaseous central ion¹. This criterium, however, can no longer be considered to be valid, as it has been shown² that an "ionic" model of the same complex certainly also could lead to diamagnetism. The actual bonding in the compounds is therefore likely to be one in between these two extremes.

We will try to show that it seems possible to indicate the "degree of covalency" for a number of diamagnetic hexacoordinated Co(III)- and Rh(III)-compounds. Further, the qualitative explanation of the variation in the measured susceptibilities in the series of Co(III)-nitroammines suggested by Asmussen³ is in accordance with the present theory. The experimental results have all been taken from the long series of measurements on Co(III)- and Rh(III)-complexes earlier carried out by one of us^{3,4}.

THEORY

Van Vleck⁵ has shown that for a diamagnetic substance the following formula holds for the measured molar susceptibility χ_M :

$$\chi_M = \frac{2}{3} N \left(\frac{e}{2mc} \right)^2 \sum_n \frac{|(n^* | \vec{L} | o)|^2}{E_n - E_0} - \frac{Ne^2}{6mc^2} \sum_q \frac{r_q^2}{r_q^3}$$

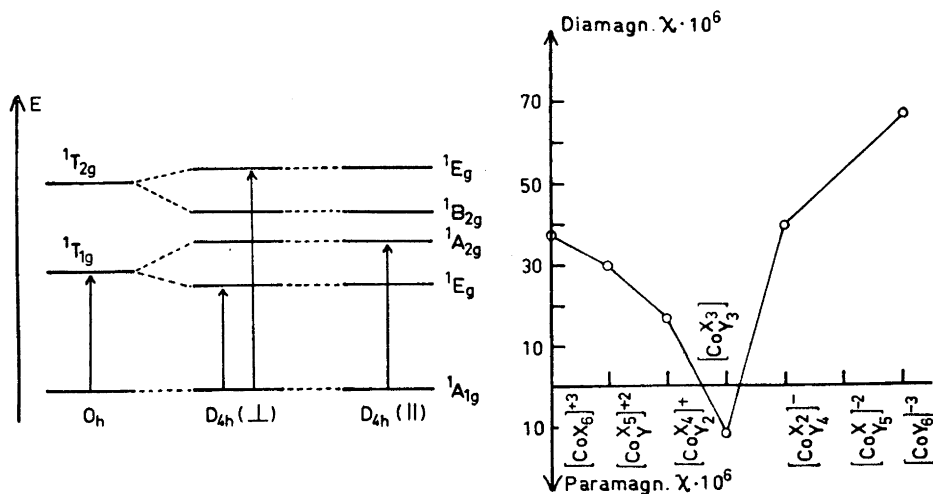


Fig. 1. The various levels and allowed magnetic dipole transitions for diamagnetic Co(III) and Rh(III) complexes.

Fig. 2. The variation of the "paramagnetic increment" by substitution. The compounds are $\text{CoX}_n\text{Y}_{4-n}$ with $\text{X} = \text{NH}_3$ and $\text{Y} = \text{NO}_2^-$. The figure is taken from Ref.³

Here N is Avogadro's number, E_n and E_0 the energy of the upper and the lower state, e and m the electronic charge and mass, c the velocity of light and $\overline{r_g^2}$ the mean square radius for electron number g . $M^2 = |(n^*|\vec{L}|o)|^2$ is the square of the operator representing the angular momenta (unit \hbar) as taken between the ground and the upper state. The first term in the equation gives rise to a temperature independent paramagnetism if L is able to couple ψ_n with ψ_0 ; the second term is a purely diamagnetic term.

Let us assume that the crystal field approximation is valid when dealing with complexes of the transition metals. By means of the wave-functions thus obtained it is easy to calculate the high-frequency term in Van Vleck's equation. Furthermore we would expect the results to be a good approximation at least for cubic and pseudocubic complexes. However, it is perhaps instructive to see what information can be obtained by means of symmetry arguments before we give the results of such a calculation.

In complexes of symmetry O_h the angular momenta \vec{L} transforms under T_{1g} . As the groundstate of a diamagnetic Co(III)- and Rh(III)-complex always transforms under A_{1g} in any symmetry, it follows that, in O_h , \vec{L} can only couple the ground state to an upper state of symmetry T_{1g} . Crystal field considerations⁶⁻⁷ show that such a state is found as the first excited level in diamagnetic d^6 systems, the next excited level being a T_{2g} state. Both are derived by exciting one electron from the groundstate, and as we are operating with determinantal one-electron wavefunctions, these are thus the only excited states we need to consider in the strong field approximation.

Table 1. Variation of the diamagnetic term with various ligands. All the measured magnetic susceptibilities are from Refs.^{3,4} except that of the Zn(II) complex, which was measured for this investigation by J. Potts Jensen. Details to be published later.

Compound	χ_M of naked metal ion $\times 10^6$	Calculated high term $\times 10^6$	Calculated diamagn. term $\times 10^6$
Co(ox ₃) ⁻³	-42	250	292
Co(NH ₃) ₆ ⁺³	52	198	146
Co(en) ₃ ⁺³	59	196	137
Co(CN) ₆ ⁻³	32	130	98
<i>trans</i> Co(en) ₂ Cl ₂ ⁺	69	235	166
<i>trans</i> Co(NH ₃) ₄ (H ₂ O) ₂ ⁺³	67	214	147
Rh(NH ₃) ₅ Cl ⁺²	10	143	133
Rh(NH ₃) ₅ NO ₂ ⁺²	20	122	102
Rh(NH ₃) ₅ ⁺³	65	127	62
Zn(en) ₃ ⁺²	-14	0	14

If the system under consideration has tetragonal symmetry D_{4h} , the magnetic moment transforms under E_g (perpendicular to the four-fold axis) and under A_{2g} (parallel to the four-fold axis). On going from O_h to D_{4h} symmetry the degeneracy of the excited states is partially removed: $T_{2g} \rightarrow B_{2g} + E_g$ and $T_{1g} \rightarrow A_{2g} + E_g$. Therefore the magnetic moment can couple the groundstate to three of the four states; A_{2g} (\parallel) and the two E_g (\perp) (cf. Fig. 1). Because of the different selection rules we would predict the magnetic susceptibility in diamagnetic Co(III) and Rh(III) complexes having tetragonal symmetry to be rather anisotropic.

The actual calculation gives⁹ that in O_h symmetry $M^2 = 24 \hbar^2$ for the ${}^1A_{1g}$ to ${}^1T_{1g}$ transition. With no account taken of the interaction between the two E_g states, and with the wavefunctions given by Ballhausen and Moffitt¹⁰ we obtain for D_{4h} : $M^2 = 16 \hbar^2$ for the transition ${}^1A_{1g}$ to ${}^1E_g(T_{1g})$, $M^2 = 8 \hbar^2$ for ${}^1A_{1g}$ to ${}^1A_{2g}(T_{1g})$ and $M^2 = 0 \hbar^2$ for ${}^1A_{1g}$ to ${}^1E_g(T_{2g})$. The energy differences are taken from the absorption spectra^{11,12} and hence we can calculate the high-frequency term in the formula. It is interesting to notice that in D_{4h} symmetry the value of the "parallel" high-frequency term is exactly one third of the value for the high-frequency term in O_h symmetry; the denominator in the expression is namely equal for these two transitions¹⁰.

We are interested in the diamagnetic term which can be obtained if the calculated high-frequency term is subtracted from the measured molar susceptibility of the gaseous metal-ion. The results are given in Table 1. The measured molar susceptibilities are all taken from Refs.^{3,4} and corrected according to the prescriptions given there.

CONCLUSIONS AND DISCUSSION

It is seen from the table that the pure diamagnetic term is highly dependent upon the nature of the various ligands, having a maximum with oxalate and a minimum with cyanide as ligands. This sequence follows the spectrochemical series very closely. According to the crystal field theory we would

expect the diamagnetic term to be nearly independent of the nature of the different ligands. As this is not the case we must conclude that the complexes under consideration have at least partially "covalent" bonds. This result must then of course be taken into consideration in a recalculation of the high-frequency term. However, this is estimated to produce only a small correction of the previous calculated numbers, which is unable to change these to any considerable extent.

A reasonable explanation of the table seems thus to be that more and more electrons are donated from the ligands to the metal ion when going from oxalate towards cyanide. Ultimately a closed shell of e_g -electrons may be obtained, having the effect of lowering the diamagnetic term of the gaseous ion. This explanation is confirmed by the value of the diamagnetic term for Zn(II) complexes. Zn complexes have a filled d-shell with virtually no high-frequency term, and these compounds are seen to have a very small diamagnetic term.

Given a hexacoordinated diamagnetic Co(III)- or Rh(III)-complex with two different kinds of ligands, X and Y, placed in this sequence in the spectrochemical series. Then it seems qualitatively possible to explain the found variation³ of the "paramagnetic increment" with substitution (*cf.* Fig. 2). As the symmetry is lowered from CoX_6 to CoX_4Y_2 and further to CoX_3Y_3 the high-frequency term in Van Vleck's formula must increase, firstly because all the higher levels can be coupled *via* L to the groundstate in the resulting low symmetry and secondly because of the depression in energy of some of the levels. By again increasing the symmetry to CoX_2Y_4 and further to CoY_6 the high-frequency term decreases again. This behaviour is just found for the measured values of the molar susceptibilities of the Co(III) nitro-ammines (Fig. 2). Both NH_3 and NO_2^- have the same value for their diamagnetic corrections so by a comparison of the different compounds this correction does not disturb. Finally we have a higher value of the molar diamagnetic susceptibility in $\text{Co}(\text{NO}_2)_6^{-3}$ than in $\text{Co}(\text{NH}_3)_6^{+3}$ because $E_a - E_0$ is greater in the former than in the latter case.

Thus there seems to be a close correspondence between the measured diamagnetism and the amount of electrons donated to the transition metal central ion. The closer the magnetism of the compounds is to that of the corresponding Zn(II) complexes, the more "covalent" they seem to be.

In this note we have followed the usual convention in assuming the diamagnetic susceptibilities of the ligands to remain unaltered by complex formation. This is probably not a very good assumption as the final analysis depends upon differences between numbers of nearly the same order of magnitude. Nevertheless, we feel that the tendency, being also what one would expect from chemical considerations, is too pronounced to be purely accidental.

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