Magnetic Susceptibility Studies and Possible Ground State Crystal Field Splitting of Two Organometallic Neptunium(IV) Complexes

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Extensive paramagnetic susceptibility studies between liquid helium and room temperature have been carried out on polycrystalline samples of the two organometallic Np(IV)-complexes $Np(C_5H_5)_4$ and $(C_5H_5)_3NpCl$. From a combined interpretation of the corresponding $1/\chi_m$-vs-T- and μ_{eff}^2-vs-T-curves, respectively, is suggested that, in accordance with the tetrahedral molecular symmetry to be assumed for $Np(C_5H_5)_4$, a cubic Γ_8 crystal field level should lie lowest in this compound. The zero field splitting is apparently smaller than 5 cm^{-1}.

From recent magnetochemical studies of two organometallic plutonium(III) compounds[1], as well as of uranium (IV) tetracyclopentadienide[2], and of some of its derivatives[3], it has become apparent that the electronic structure of many $5f^n$-systems might be better elucidated by their magnetism than that of related $4f^n$-systems[4, 5]. In cases favourable particulary, further improvement of the interpretation of susceptibility data over a sufficiently large temperature range becomes possible by consideration of the familiar $1/\chi_m$-versus-T-diagrams on the one hand, together with corresponding plots of the quantity $2{,}828^2 \cdot \chi_m \cdot T = \mu_{eff}^2$ versus T on the other. As usual, χ_m is the molar magnetic susceptibility, T the absolute temperature and μ_{eff} the effective magnetic moment. The latter representation of magneto-chemical data was recommended briefly by SCHLAPP and PENNEY as early as in 1932[6, 7], but so far hardly any practical use has been made of it.

The aim of the present study dealing with neptunium (IV)-tetracyclopentadienide, $Np(C_5H_5)_4$ (= $NpCp_4$)[8], and triscyclopentadienyl-neptunium-(IV) chloride, $(C_5H_5)_3NpCl$ (= Cp_3NpCl)[9], is twofold: First, there is still a dearth of information about the magnetochemistry of Np(IV) compounds in general, not to speak of the rather unconventional organometallic species. Secondly, these two compounds appear also well-suited to provide further information on the effectiveness of the μ_{eff}^2-vs-T-representation and the conclusions to be drawn from it. By analogy with UCp_4[2], the molecular symmetry of $NpCp_4$ may be considered essentially tetrahedral, focussing particular interest upon the electronic structure of this compound.

Apart from a rather extensive paper on $KNp(IV)F_5$[10], and from apparently still unpublished results from other laboratories[11], only two further magnetic susceptibility studies of Np(IV)-compounds covering more than three different temperatures have

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[1] R. D. FISCHER, P. LAUBEREAU, and B. KANELLAKOPULOS, presented at the Westdeutsche Chemiedozententagung **1968**, Hamburg (to be published).

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[3] R. D. FISCHER, P. LAUBEREAU, R. v. AMMON, and B. KANELLAKOPULOS, in press.

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[5] P. LAUBEREAU and R. D. FISCHER, unpublished results on $(C_5H_5)_3Pr$ and $(C_5H_5)_3Tm$.

[6] R. SCHLAPP and W. G. PENNEY, Phys. Rev. **42**, 666 [1932].

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[9] E. O. FISCHER, P. LAUBEREAU, F. BAUMGÄRTNER, and B. KANELLAKOPULOS, J. Organomet. Chem. **5**, 583 [1966].

[10] D. M. GRUEN and C. A. HUTCHISON, JR., J. Chem. Phys. **22**, 386 [1954]. cf also Ref. [10a]

[10a] According to private communication by Dr. D. Brown, the 1:1 ratio of K to Np in this compound is questionable; its formula should rather be $K_7Np_6F_{31}$.

[11] B. P. DORAIN and C. A. HUTCHISON; cf. W. LOW, Paramagnetic Resonance in Solids, Academic Press New York and London 1960, p. 140; cf. also ref. [22].

so far been reported[12]. Conseqently in what fallows we are restricted to a comparison of our results with those for $KNpF_5$.

Experimental

Both compounds were prepared precisely as described by BAUMGÄRTNER et al.[8, 9]. Magnetic measurements were carried out on finely ground polycrystalline samples immediately after the preparation. For all magnetic measurements the Faraday method was employed, using the magnetic balance at the Tieftemperatur-Institut of the Bayerische Akademie der Wissenschaften[13, 14, 15]. This instrument permits measurements at any desired temperature between liquid helium and room temperature, making it possible to study the particularly interesting temperature range between 4.2 and ca. 100 °K with appreciable accuracy. All finer details concerning the balance and the procedure of measuring the susceptibilities have been reported elsewhere[2].

The experimental susceptibility values were corrected as usual for the diamagnetic contributions of the ligands[16]. However, for the diamagnetic contribution of the Np(IV)-ion a value of similar accuracy is not yet available. In the case of $NpCp_4$, an estimated value of -40×10^{-6} cm³/mole which lies only slightly higher than the corresponding values usually employed for Th^{4+}, U^{4+}, and Pu^{+4}, respectively, was adopted. As the final plots were not noticeably affected by this particular correction, no attempt was made to refine the Cp_3NpCl-data. Measurements at different magnetic field strengths between ca. 575 and 4390 gauss did not indicate any variation of the susceptibilities with the magnetic field strength.

The $1/\chi_m$*-vs-*T*-representation:*

Fig. 1 shows the $1/\chi_m$-vs-T-diagrams of $NpCp_4$, Cp_3NpCl, and $KNpF_5$. For further comparison the theoretical straight lines to be expected for the free ionic $^4I'_{9/2}$ ground state of Np(IV) (the primed symbol includes situations which may deviate from those to be described by pure Russell Saunders

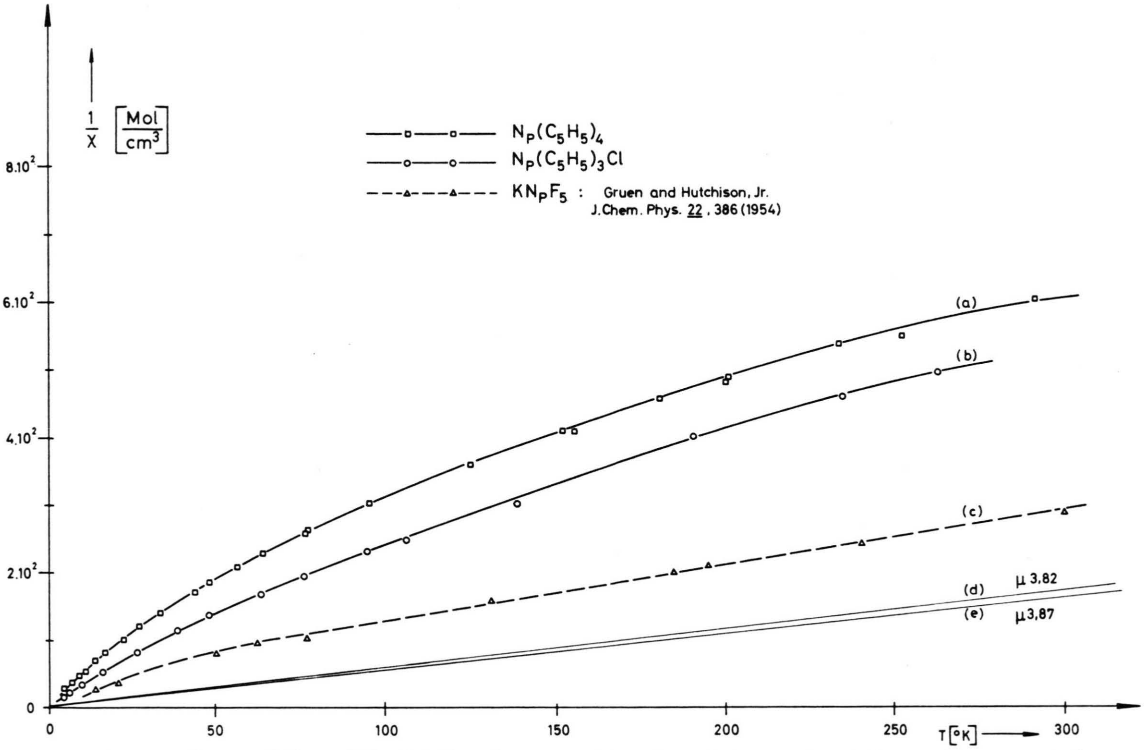

Fig. 1. Magnetic Susceptibility of Np(IV) Complexes as a Function of Temperature ($1/\chi_m$-vs-T-representation). (d): calculated for the $^4I'_{9/2}$ ground state of Np (IV) (e): "spin-only"-situation for three unpaired electrons

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[12] Thus, the complexes $Cs_2[NpCl_6]$ and $NpCl_4 \cdot 2{,}5$ DMA (DMA = dimethylacetamide) have been investigated between ca. 90 and 300°K (K. W. BAGNALL) and J. B. LAIDLER, J. Chem. Soc. (A) **1966, 516**). Recently, also the magnetism of NpO_2 has been studied (L. HEATON, H. MUELLER, and I. M. WILLIAMS, J. Phys. Chem. Solids **28**, 1651 [1967]), however, strong evidence for antiferromagnetism in this case does not permit direct comparison with our examples.

[13] H. LEIPFINGER, Z. Phys. **150**, 415 [1958].

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[15] Dr. W. WIEDEMANN from this Institut is thanked for his kind assistance.

[16] B. N. FIGGIS and J. LEWIS in: H. B. JONASSEN and A. WEISSBERGER Edts. Technique of Inorganic Chemistry **4**, 137 [1965], Interscience Publishers.

coupling) and for three unpaired electrons in the "spin-only-situation", respectively, are also included. The slope of curve (d) deviates somewhat from that expected for the ground state of the free $4f^3$-system Nd(III), since more realistic wave functions accounting for intermediate coupling[17] in Np(IV) were used to determine its appropriate Landé g-factor.

Although the two curves (d) and (e) are assigned to completely different situations, their slopes happen to be surprisingly similar.

It is seen that the curves (a) and (b), also start rather precisely from the coordinate origin, as is required for all configurations involving an odd number of f-electrons if noticeable intermolecular spin pairing phenomena may be ignored. This view seems independently justified by the actual size of each Cp-ligand, and is consistent with all previous experience of cyclopentadienyl complexes of actinide elements. While above ca. 75 °K at least partial Curie-Weiss behaviour may be ascribed to curve (c), the curves of the two organometallic compounds do not exhibit any linearity extening over reasonable temperature ranges. This behaviour may be due to the presence of at least one excited crystal field (= CF) level of the $^4I'_{9/2}$-manifold at an energy of ca. 250 ± 100 cm^{-1} above the ground level.

Furthermore, the curves of the two organometallic compounds deviate even more than curve (c) from the theoretical lines (d) and (e), both as far as the actual susceptibility values and the different slopes at various temperatures are concerned. The organic ligand systems might therefore be likely to produce a somewhat stronger crystal field splitting than the five fluorine anions in $KNpF_5$.

The μ^2_{eff}-vs-T-representation:

In Fig. 2 plots of the quantity $2{,}828^2 \cdot \chi_m \cdot T = \mu^2_{\text{eff}}$ versus the absolute temperature are shown, including again the compound $KNpF_5$. Here, the two idealized cases of the "spin-only-situation" and the free ion magnetism, respectively, are realized by straight lines parallel to the T-axis, again neglecting all contributions of the lowest excited ionic states via second order Zeeman interactions.

First of all, it is seen that the new plots again give rise to very smooth curves, emphasising the rather satisfactory consistency of the primary susceptibility data. The differences between the μ^2_{eff}-vs-T curves of $NpCp_4$ and Cp_3NpC on the one hand, and those of $KNpF_5$ and the free ion on the other, appear more pronounced than in the $1/\chi_m$-vs-T-representation. Hardly any section of the Cp_3NpCl curve may be considered linear, whereas the $NpCp_4$ curve is likely to approach linearity above 150 °K.

The most interesting feature of the $NpCp_4$-curve is its rather pronounced change of direction around ca. 10 °K (≙ 6,9 cm^{-1}). Although the curves (f) and (g) have roughly the same shape over almost the entire temperature range, there is no indication whatsoever in the Cp_3NpCl-curve of a similar bending at very low temperatures. It should be noted that no inconsistency for this evidence was obtained from the two corresponding $1/\chi_m$-vs-T-curves, either. However, similar differences hav ealso been revealed unambiguously by the respective curves of UCp_4[2] and bis-phthalocyaninato-uranium(IV)[18,19], confirming thus an occasional superiority of μ^2_{eff}-vs-T-plots over the $1/\chi_m$-vs-T-representations at low temperatures. To explain the directional change of curve (g), the assumption of *inter*molecular spin coupling seems rather unrealistic, this kind of interaction being even less likely for $NpCp_4$ than for Cp_3NpCl, due to the very bulky ligand sphere almost completely enveloping the central ion. We are therefore essentially left with the assumption of a CF-splitting pattern involving one extremely low-lying excited state.

Provided that the very low-lying first excited state of $NpCp_4$ is thermally populated to $\geqq 48\%$ at 20 °K, by application of a simple Boltzmann distribution (this rough estimate implies that both levels are Kramers-doublets, and neglects the influence of all higher CF-levels) the separation δ of this level from the ground state may be caculated to be $\leqq 1{,}5\ \text{cm}^{-1}$. If there were no other CF-levels located ca. 250 cm^{-1} (below corresponding roughly to room temperature) the μ^2_{eff}-vs-T-curve of $NpCp_4$ should be approximately linear. However, the average slopes between 20 and 70 °K on one hand, and between 200 and 300 °K on the other, differ con-

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[17] J. G. CONWAY, J. Chem. Phys. **41**, 904 [1964]. — We are greatly indebted to Professor J. G. CONWAY for supplying us with the appropriate eigenvectors of the ionic states of Np(IV).

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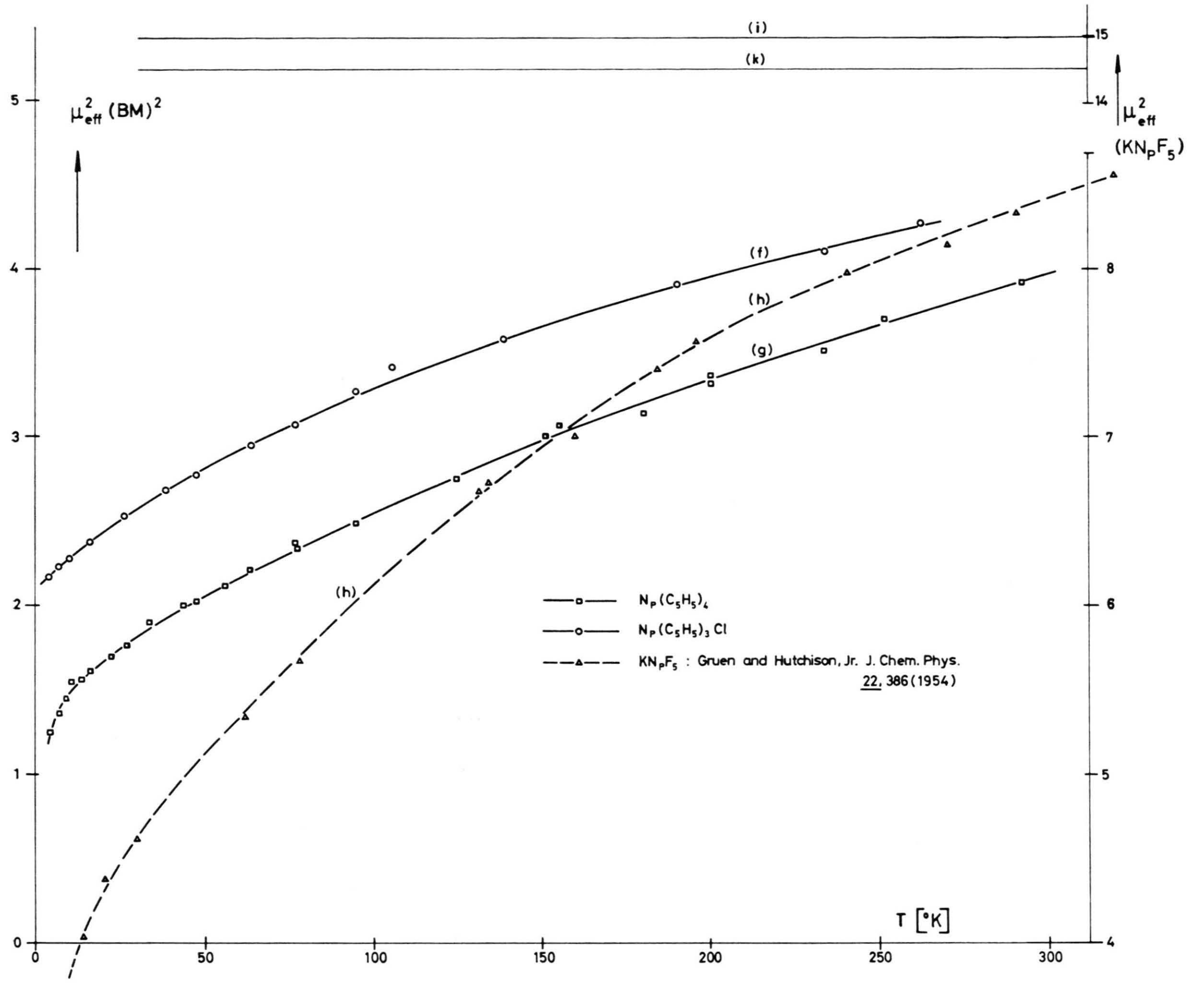

Fig. 2. Magnetic Moments of Np(IV) Complexes as a Function of Temperature (μ^2_{eff}-vs-T-representation). Curve (i) corresponds tocurve (e). and (k) to curve (d) in Fig. 1. Note that there is a break between $\mu^2_{eff} = 9$ and 14 [B.M.]^2.

siderably, suggesting again that at least one more CF-level may be located around 150 cm^{-1}.

Discussion and Conclusions:

For a tetrahedral arrangement of the four Cp-ring normals in NpCp$_4$, the ionic ground level of Np(IV) with $J = 9/2$ will be split into only three CF-levels, two of which belong to the fourfold degenerate irreducible representation $^4\Gamma_8$ of the cubic double group[20], and one being a normal Kramers-doublet $^2\Gamma_6$. The very narrow spacing of the two lowest states could then be explained resonably in terms of additional splitting of an originally tetrahedral level rather than by some accidental degeneracy. Only a $^4\Gamma_8$ state may undergo further splitting in the absence of external magnetic fields. In principle, at least a small ,,zero field splitting,, is expected by the Jahn-Teller-theorem. In addition, by the lack of *three*-fold-rotational symmetry around the four Cp-ring axes, no ideal tetrahedral arrangement of the individual C- and H-atoms of the ligands is achieved. From the generalized CF-splitting diagram for a $J = 9/2$ manifold in cubic symmetry as given by LEA, LEASK, and WOLF[21], it is immediately seen that f^3-systems may readily possess a cubic $^4\Gamma_8$ ground

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[20] H. BETHE, Ann. Phys. **3**, 133 [1929].

[21] K. R. LEA, M. J. M. LEASK, and W. P. WOLF, J. Phys. Chem. Solids **23**, 1381 [1962].

level. This diagram indicates further that each possible situation of accidental degeneracy also involves one $^4\Gamma_8$ state.

Experimentally, $^4\Gamma_8$ ground levels habe so far hardly been verified in systems with cubic symmetry. Concerning the Zeeman splitting of this kind of CF-level[22] the same isotropic behaviour as for cubic Kramers doublets is no longer expected. Nevertheless, as long as the inequality: $kT \gg \beta H$ is maintained (k being Boltzmann's constant, β the Bohr magneton and H the magnetic field strength), the susceptibility may be regarded as isotropic and will follow Curie's law (Bleaney[22]). Clearly, the unusual properties of a $^4\Gamma_8$-level would not vanish immediately when additional CF-splitting begins. However, all information obtained from static susceptibility measurements on polycrystalline samples will not be powerful enough to serve as a final proof for any residual or even pure $^4\Gamma_8$-character. In this particular case, electron spin resonance studies, even of polycrystalline samples, would appear more promising. Such studies together with the evaluation of the approximate the cubic CF-splitting parameters of $NpCp_4$ are presently in progress.

Acknowledgements

The authors are grateful to Professors F. Baumgärtner and E. O. Fischer for their interest in this work, and to Messrs. E. Dornberger and H. Billich for their technical assistance. R.D.F. is further indebted to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial help, and P. L. to the German Bundesministerium für Wissenschaftliche Forschung.

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Negative magnetische Widerstandsänderung von ZnSb

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ZnSb zeigt wie einige andere Halbleiter bei tiefen Temperaturen die eigenartige Erscheinung einer negativen magnetischen Widerstandsänderung, d. h. eine Abnahme des elektrischen Widerstandes im Magnetfeld. Die Größe dieses Effektes wurde in Abhängigkeit vom Magnetfeld H und von der Ladungsträgerkonzentration p untersucht. Für das Auftreten der Erscheinung können Grenzen in bezug auf p und H angegeben werden. Die Messungen an einkristallinem und polykristallinem Material zeigen unterschiedliche Resultate. Die Ergebnisse werden vor allem in bezug auf verschiedene Komponentenzerlegung in positive und negative Anteile der Widerstandsänderung diskutiert.

1. Einleitung

Neben der gewöhnlichen positiven magnetischen Widerstandsänderung wurde in den letzten Jahren bei verschiedenen Halbleitern (Ge, Si, GaAs, SiC, InSb, CdS) eine negative magnetische Widerstandsänderung, d. h. eine Abnahme des Widerstandes im Magnetfeld gefunden. Diese Erscheinung konnten wir auch beim ZnSb bei tiefen Temperaturen feststellen[1]. Im folgenden wird über die Abhängigkeit dieses Effektes beim ZnSb von verschiedenen Parametern berichtet.

2. Probenmaterial und Meßeinrichtung

Die Herstellung von polykristallinem und einkristallinem Material der II-V-Verbindung ZnSb wurde schon in vorhergehenden Arbeiten beschrieben[2, 3, 4]. Die Ausgangsmaterialien hatten eine Reinheit von 99,9999%. Proben mit verschiedener Defektelektronenkonzentration p ergaben sich durch entsprechende Cu-Dotierung. Die Probenabmessungen waren ca. $3 \times 3 \times 10$ mm^3. Kontakte wurden mit In-Sn-Lot angebracht. Die Proben wurden in einen Glas-Kryostaten zwischen den Polschuhen

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