Magnetic susceptibility of some organometallic compounds of neptunium (IV)
A. Stollenwerk, R. Klenze, B. Kanellakopulos

To cite this version:
A. Stollenwerk, R. Klenze, B. Kanellakopulos. Magnetic susceptibility of some organometallic compounds of neptunium (IV). Journal de Physique Colloques, 1979, 40 (C4), pp.C4-179-C4-180. <10.1051/jphyscol:1979456>. <jpa-00218852>

HAL Id: jpa-00218852
https://hal.archives-ouvertes.fr/jpa-00218852
Submitted on 1 Jan 1979

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Magnetic susceptibility of some organometallic compounds of neptunium (IV)

A. H. Stollenwerk, R. Klenze and B. Kanellakopoulos


Résumé. — Les composés du neptunium tétravalent avec le cyclopentadiényle, (C₅H₅)₃NpX (X = F, Cl, Br, I, (SO₄)₁/2, ont été préparés et étudiés. Nous discutons les mesures de susceptibilité magnétique dans le domaine de températures de 1 K à la température ambiante. Cette analyse donne des informations relatives au niveau électronique fondamental 1/L₂ du cation Np(IV) sous l'influence du champ des ligands.

Abstract. — A series of cyclopentadienyl compounds of the tetravalent neptunium, (C₅H₅)₃NpX with X = F, Cl, Br, I, (SO₄)₁/2, have been prepared and investigated. Magnetic susceptibility measurements of all compounds in the temperature range from room temperature down to 1 K give information about the electronic ground state 1/L₂ of the Np(IV)-ion split by crystal field. The temperature dependence of the magnetic susceptibility of the complexes is discussed.

1. Introduction. — In recent years considerable progress has been made in the interpretation of the physico-chemical properties of a series of (C₅H₅)₃UX compounds with a large variation in the ligand X. Although these compounds have rather poor symmetry, it has been shown that a restricted set of calculation parameters is sufficient for a simultaneous interpretation of spectroscopic, magnetic susceptibility and NMR spectroscopic data [1].

Contrary to the (C₅H₅)₃UX compounds which have a non-magnetic ground state, the analogous neptunium compounds are expected to have a magnetic ground state, which provides additional information from magnetic measurements at low temperatures.

This has been demonstrated for the highly symmetric actinide compounds [(C₂H₅)₄N]₄An(NCS)₉ [2, 3], with An = Th, U, Np. While in the case of the uranium compound the electronic ground state is strongly affected by Jahn-Teller distortion, the electronic ground state of the neptunium complex is not distorted.

This fact leads us to the conclusion that studies on the (C₅H₅)₃NpX series should be even more promising.

2. Preparation of the compounds. — The (C₅H₅)₃NpX compounds, where X = Cl, Br, I, (SO₄)₁/2, were prepared by reacting Np(C₅H₅)₄ with a stoichiometric amount of the respective ammonium salts [4]. The starting material, Np(C₅H₅)₄, was prepared from the reaction of NpCl₃ with an excess of K(C₂H₅) [5]. (C₅H₅)₃NpF was obtained by reacting a mixture of (C₅H₅)₃NpCl with an excess of NaF at 300 °C for 40 hours in a sealed glass tube and then extracting with tetrahydrofuran.

3. Magnetic susceptibility measurements. — Magnetic susceptibility data on all the neptunium compounds were obtained from 300 K down to 1 K by using a Faraday magnetic balance.

With the exception of (C₅H₅)₃NpF, all compounds show a very similar behaviour in this temperature range (see Fig. 1).

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:1979456
A. H. STOLLENWERK, R. KLENZE AND B. KANELLAKOPULOS

a) Between 15 and 100 K the temperature dependence of $\mu_{\text{eff}}^2 = 8.00 \chi T$ is a straight line corresponding to a second order Zeeman effect of the ground level with the next excited Stark component of the $^4l_{9/2}$ multiplet split by the crystal field.

b) Below 15 K the magnetic susceptibility of all compounds becomes field dependent as expected for magnetically active electronic ground states. A slight deviation of the magnetization curves from the Brillouin function was observed in the temperature region below 4 K.

c) Above 100 K at least one more Stark level becomes thermally populated, but up to 300 K the free ion $^4l_{9/2}$ magnetism is by far not reached.

The magnetic susceptibility curve of $(C,H_5)_2\text{NpF}$ differs considerably from those of its halide homologues and suggests that self-association possibly occurs, as has been shown for $(C,H_5)_2\text{UF}$ [6].

4. $^1H$-NMR-investigations. — Nuclear magnetic resonance data for the cyclopentadienyl ring protons of actinide cyclopentadienyl compounds offer even more difficulties for interpretation, since while one of the two forms which contribute to the paramagnetic displacement varies with the magnetic susceptibility, the other term is proportional to the anisotropy of the magnetic susceptibility.

Our data obtained on $(C,H_5)_2\text{NpX} (X = \text{Cl}, \text{Br}, \text{I})$, for the inverse paramagnetic displacement versus temperature, show a Curie-Weiss behaviour above 240 K up to 340 K and indicate a normal Curie behaviour below 240 K down to 210 K.

References
Marks, T., Kolb, J. R., J. Am. Chem. Soc. 97 (1975) 27;