Journal of Alloys and Compounds 275–277 (1998) 798–800

Synthesis and magnetic properties of $(C_5H_5)_3Ce{\cdot}HMPA$

E.M. Aricó[a,*], B. Kanellakopulos[b], C. Apostolidis[c], L.B. Zinner[a]

[a] *Instituto de Química, Universidade de São Paulo, Caixa Postal 26.077, CEP 005599-970, São Paulo SP, Brazil*

[b] *Institut für Technische Chemie, Bereich chemisch-physikalische Verfahren, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021, Karlsruhe, Germany*

[c] *European Commission, Joint Research Centre, Institut for Transuranic Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

Abstract

The 1:1 adduct $(C_5H_5)_3Ce{\cdot}O{=}P(NMe_2)_3$ of cerium(III)-triscyclopentadienide with hexamethylphosphoric triamide (HMPA) was synthesized, isolated, purified and characterized by elemental analysis, IR- and ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum obtained in solution in $CDCl_3$ at room temperature exhibits a single signal for the Cp-proton at 5.6 ppm and a signal for the CH_3-proton of the base HMPA at 0.49 ppm. The paramagnetic shift due to the Ce(III) ion could be evaluated by comparison to the corresponding signals of the homologous diamagnetic compound $Cp_3La{\cdot}HMPA$. The temperature-dependent paramagnetic susceptibility of the compound was measured within the temperature range from 4.2 up to 300 K. From the $1/\chi_{mol}$ vs. T-plot the empirical constant $C=0.78$ m^3 K mol^{-1} was evaluated with a Curie-Weiss constant θ of -71 K. The temperature dependence of the magnetic moment (μ_{eff}) is consistent with a Ce(III) ion. The ground state of the Ce ion is only partially populated. The magnetic moment at room temperature is 2.25 μ_B, an indication of covalency, as it has been observed for several Ce(III)-organometallics. © 1998 Elsevier Science S.A.

Keywords: Organolanthanide; Cerium(III); Hexamethylphosphoramide; Cerium-triscyclopentadienide

1. Introduction

Adducts of lanthanide cyclopentadienides with Lewis bases have been described in the literature concerning structural and spectroscopic studies [1–4].

Although the Ce(III) ion has the simple [Xe]4f^1 electronic configuration, its organometallic compounds have not been frequently employed for investigation of the f-f transitions so far. As a consequence of its accessible 4+ oxidation state, the organometallic compounds of trivalent cerium are extremely air sensitive. Moreover the f-f electron transition in these ion occurs at the infrared and far infrared range which makes difficult its observation [5].

The study of proton magnetic resonance together with magnetic susceptibility measurements are very useful in the evaluation of the crystal field levels of the trivalent cerium ion [6]. The comparable ionic radii of the trivalent cerium and lanthanum and the similarity of the molecular structures in homologous compounds of the two ions enables the use of the experimental data of the diamagnetic lanthan(III) compounds to evaluate the paramagnetic shift in the NMR spectrum.

2. Experimental

The compounds Cp_3Ce and $Cp_3Ce{\cdot}HMPA$ (HMPA= hexamethylphosphoric triamide) are extremely air and moisture sensitive; therefore all operations for the synthesis, characterization, and investigation were carried out under an atmosphere of purified argon gas using Schlenk-tube techniques. Pentane, used as solvent in the synthesis and purification, was refluxed over calcium hydride and distilled under argon just prior to use. The ligand HMPA was purified by vacuum distillation over calcium hydride and kept under argon atmosphere.

The IR spectrum in the range of 4000 to 250 cm^{-1} was registered on a sample in solid state in a matrix of potassium bromide for the $Cp_3Ce{\cdot}HMPA$ and between NaCl plates for the liquid ligand HMPA with a Perkin-Elmer-283 infrared spectrometer.

The ^{1}H-NMR spectra were run at room temperature with a Bruker 250 MHz AC250 NMR-Spectrometer in CD_3Cl solutions (99%D, Merck); TMS was used as internal standard.

Magnetic susceptibility measurements were performed with a Faraday-magnetic balance at external magnetic fields between 190 and 15 000 Oe. It consists of a

---

[*] Corresponding author.

PII: S0925-8388(98)00444-7

microbalance Sartorius Typ 4102 and a Magnet Bruker B-E-25 C8. The measurements were carried out in the temperature range between 4.2 and 300 K.

2.1. Synthesis of Cp_3Ce·HMPA

In a Schlenk flask containing 0.4695 g (1.40 mmol) Cp_3Ce about 25 ml of freshly distilled *n*-pentane were added. The equimolar amount of HMPA, 0.250 ml (0.2509 g≈1.40 mmol) was dropped to this suspension. After stirring overnight at room temperature and complete solvent elimination by distillation under vacuo, the dried product was extracted with *n*-pentane. The pale beige polycrystalline compound Cp_3Ce·HMPA was isolated after removal of the solvent by decantation and dried under vacuo.

3. Results and discussion

The 1:1 stoichiometry of the adduct Cp_3Ce·HMPA was satisfactorily confirmed through the results of elemental analyses (Table 1).

In the IR spectrum the bands assigned to the Cp^- anion appear at 3087(w), 1464(w), 1125(m), 1014(s) and 771(s) cm^{-1} and are consistent with the η^5 coordination mode of the cyclopentadienyl ring to the metallic centre. The coordination of the Lewis base HMPA could be inferred from the shift of the band assigned to the $\nu_{P=O}$ stretching vibration to lower energy, at 1190 cm^{-1} for the cerium compound and at 1203 cm^{-1} for the free base. This shift occurs as a result of the electrons withdrawing from the coordinating oxygen atom of the ligand to the metal cation. This reduces the double bond character of the P=O interaction and consequently extends its length and diminishes its vibrational energy.

The ^{1}H-NMR spectrum of the Cp_3Ce·HMPA adduct was analyzed in comparison to those of the diamagnetic analogous Cp_3La·HMPA. The signals for the HMPA methyl groups in the spectrum of the diamagnetic Cp_3La·HMPA exhibit a doublet at 2.78 and 2.74 ppm (2.67 and 2.63 ppm for the free ligand HMPA). The protons of the Cp^- rings appear as a singlet at 6.00 ppm. The corresponding signals in the spectrum of the Cp_3Ce·HMPA appear at 0.49 ppm (CH_3-groups) and at 5.6 ppm (Cp-ring-protons).

The singlet of the CH_3 protons indicates that the $P[N(CH_3)_2]_3$ moiety of the HMPA molecule is free rotating around the threefold Ln–O–P axis. The effect of the paramagnetic Ce(III) ion over the resonance of the HMPA methyl group causes a broadening of its signal ($\nu_{1/2}$=38.3 Hz) that overcomes the P–H coupling, seen as a doublet signal at the diamagnetic La(III) adduct and at the uncoordinated HMPA.

Table 1
Calculated and experimentally found elemental analysis

	%Ce	%C	%H	%N	%P
Calc.	27.23	49.01	6.46	8.16	6.02
Found	28.10	48.94	6.72	8.40	6.18

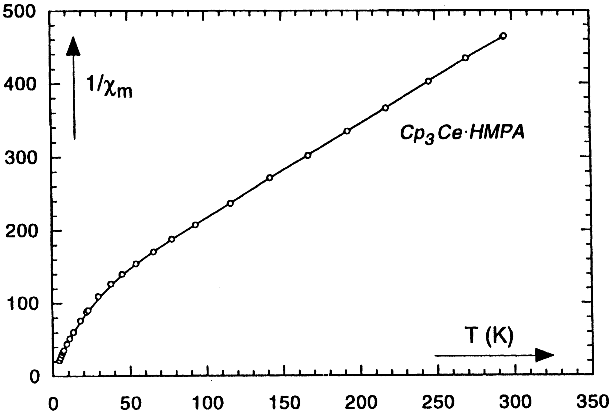

Fig. 1. Reciprocal molar susceptibility, $\chi_{M^{-1}}$, as a function of *T*.

The single signal for all 15 protons of the three Cp^- rings, observed in both 1:1 adducts of La(III) and Ce(III), underlines the pentahapto-coordination of the Cp^- rings and their equivalent position around the metal cation.

The magnetic susceptibility of the solid polycrystalline Cp_3Ce·HMPA was measured within the temperature range from 4.2 to 300 K. The plot of the reciprocal molar susceptibility $\chi_{M^{-1}}$ as a function of *T* is shown in Fig. 1. Within the investigated temperature range two parts of the curve can be observed:

1. in low temperature range from 4.2 to 70 K, the $\chi_{M^{-1}}$-vs. *T* curve is not linear;
2. in the high temperature range from 70 to 300 K, $\chi_{M^{-1}}$ is linear in temperature and obeys the Curie-Weiss law ($\chi_{M^{-1}}=(T-\theta)/C$). The slope of the plot $\chi_{M^{-1}}$ vs. $-T$ gives a *C*-value of 0.78 m^3 K mol^{-1} (Table 2). The empirical constant θ (the extrapolated intercept) was also evaluated. The *C*- and θ-values are comparable with those of other Cp_3Ce adducts ([7], Kanellakopulos et al., unpublished results). The similarity of the respective empirical constant *C* and θ of the investigated Ce(III) adducts is due to the fact that in all compounds the cerium ion is in a similar symmetry and the chemical environment is affected only by the influence of the different Lewis bases.

Table 2
Empirical constants *C* and θ observed for Cp_3Ce·B adducts

CpCe·HMPA B	*C* m^3.K.mol^{-1}	θ K
HMPA	0.78	−71
THF (Kanellakopulos et al., unpublished results)	0.82	−42
$NCCH_3$ [7]	0.76	−46
CNC_6H_{11} [7]	0.71	−27

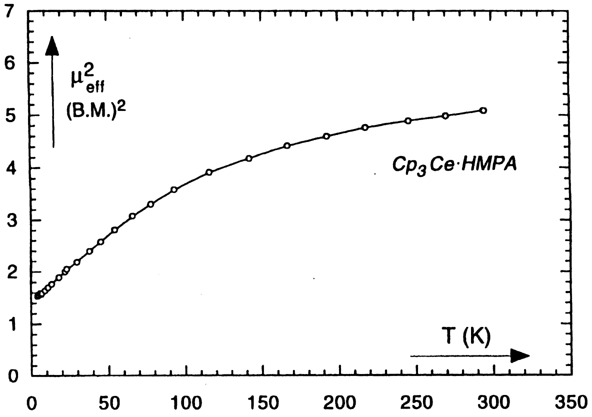

Fig. 2. Effective magnetic moment, μ_{eff} in the temperature range from 4.2 to 300 K.

The temperature dependence of the effective magnetic moment (μ_{eff}) in the temperature range from 4.2 to 300 K is shown in Fig. 2. At low temperatures the values of μ_{eff} of $Cp_3Ce \cdot HMPA$ are comparable with those observed in the adducts of $Cp_3Ce \cdot B$ with the Lewis bases THF, $CNCH_3$, and CNC_6H_{11} [7]. Taking into account that all these 1:1 adducts have comparable symmetry, it can be assumed that for the $Cp_3Ce \cdot HMPA$ adduct, in the case $T \rightarrow 0$, the population of the crystal field levels of the cerium ion occurs at the Kramer doublet, which corresponds to $J=3/2$ [8,9].

The positive slope of the curve is a consequence of the population of the excited levels of the ground term $^2F_{5/2}$, however even at room temperature the saturation of these levels is not achieved. A complete population of the excited crystal field levels could show a plateau in the curve.

The magnetic moment, μ_{eff}, observed for the $Cp_3Ce \cdot$ HMPA adduct at room temperature is 2.25 μ_B. This value is somewhat lower than the value 2.54 μ_B predicted by Van Vleck [10] for the free Ce(III)-ion. The deviation can be considered as an indication for covalence as it has been already observed in several Ce(III) organometallic compounds [6].

4. Conclusions

In the $Cp_3Ce \cdot HMPA$ adduct the Ce(III) ion is surrounded by three η^5-coordinated cyclopentadienide rings in equivalent positions, symmetrically to the threefold axis of the molecule. The Ce–O=P-bond is on the threefold axis and the $[N(CH_3)_2]_3$ moiety rotates free.

The empirical θ and Curie-Weiss constants evaluated from the temperature-dependent paramagnetic susceptibility are comparable with the corresponding values of several other 1:1 adducts of $CeCp_3$ with Lewis bases, which indicates that they all may have analogous symmetry.

The effective magnetic moment μ_{eff} at room temperature is lower than that calculated for the free Ce(III) ion, which can be considered as a result of the covalent contribution at the Ce–C interaction.

Acknowledgements

The financial support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and of the Deutscher Akademischer Austauschdienst (DAAD) is gratefully acknowledged.

References

[1] E.O. Fischer, H. Fischer, J. Organometal. Chem. 6 (1966) 141–148.
[2] L. Xing-Fu, S. Eggers, J. Kopf, W. Jahn, R.D. Fischer, C. Apostolidis, B. Kanellakopulos, F. Bnetollo, A. Polo, G. Bombieri, Inorg. Chem. Acta 100 (1985) 183–199.
[3] C. Apostolidis, B. Kanellakopulos, R. Klenze, H. Redmann, H. Schultz, H.D. Amberger, J. Organometal. Chem 426 (1992) 307–323.
[4] B. Kanellakopulos, R. von Ammon, C. Apostolidis, E. Dornberger, R. Maier, J. Müller, X. Zhang, J. Organometal. Chem. 483 (1994) 193–204.
[5] G.H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, Interscience, New York, 1968.
[6] H. Redmann, H. Schultze, H.D. Amberger, C. Apostolidis, B. Kanellakopulos, Spectrochim. Acta 46A (1990) 1223–1229.
[7] C. Apostolidis, Dissertation, Universität Heidelberg, 1982.
[8] B. Kanellakopulos, R. Klenze, KFK Nachr. 16 (1984) 119–122.
[9] R. Klenze, Dissertation, Universität Heidelberg, 1995.
[10] J.H. van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, Oxford, 1932, p. 239.