9/1). The eluates were evaporated to dryness in vacuo (ca. 0.1 mbar), and the residues recrystallized from *n*-pentane/toluene (9/1). Selected physical and NMR spectroscopic data for **5a**, **b** (the deuterated solvents were used as internal and 85% H_3PO_4 as external standards). **5a**: yellow powder, yield: 180 mg (34%), m.p. 113 °C (decomp). **5a**: $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25 °C): $\delta = 20.3$ (d, ^1J(P,C) = 27.1 Hz; P*C*H$_3$), 24.2 (s; NCC*C*H$_2$), 25.7 (s; NC*C*CH$_2$), 48.5 (s; N*C*CCH$_2$), 52.3 (s; OMe), 52.8 (s; OMe), 141.6 (d, $^{(2+3)}J$(P,C) = 21.1 Hz; PC*C*), 159.7 (d, $^{(1+4)}J$(P,C) = 8.4 Hz; P*C*C), 160.2 (d, $^{(2+3)}J$(P,C) = 5.4 Hz; PN*C*), 161.4 (d, J(P,C) = 11.1 Hz; *C*O$_2$Me), 165.6 (d, J(P,C) = 15.4 Hz; *C*O$_2$Me), 196.5 (d, ^2J(P,C) = 7.6 Hz; *cis*-CO), 199.8 (d, ^2J(P,C) = 21.7 Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): $\delta = 76.0$ (s, ^1J(P,^{183}W) = 248.7 Hz). **5b**: yellow powder, yield: 80 mg (13%), m.p. 124 °C (decomp). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 25 °C): $\delta = 24.3$ (s; NCC*C*H$_2$), 25.9 (s; NC*C*CH$_2$), 48.9 (s; N*C*CCH$_2$), 52.8 (s; OMe), 53.4 (s; OMe), 128.7 (d, ^2J(P,C) = 10.6 Hz; *o*-Ph), 130.8 (d, ^3J(P,C) = 14.1 Hz; *m*-Ph), 131.2 (d, ^4J(P,C) = 2.9 Hz; *p*-Ph), 131.9 (d, ^1J(P,C) = 42.1 Hz; *i*-Ph), 140.0 (d, $^{(2+3)}J$(P,C) = 20.4 Hz; PC*C*), 159.3 (d, $^{(1+4)}J$(P,C) = 7.6 Hz; P*C*C), 160.9 (d, $^{(2+3)}J$(P,C) = 5.4 Hz; PN*C*), 161.4 (d, J(P,C) = 10.8 Hz; *C*O$_2$Me), 165.6 (d, J(P,C) = 15.3 Hz; *C*O$_2$Me), 196.0 (d, ^2J(P,C) = 6.4 Hz; *cis*-CO), 199.0 (d, ^2J(P,C) = 22.8 Hz; *trans*-CO); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 25 °C): $\delta = 78.8$ (s, ^1J(P,^{183}W) = 254.0 Hz).

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[11] Crystal structure analysis of complex **5a**: $C_{18}H_{19}N_2O_9PW$, $M_r = 622.17$; monoclinic, space group $P2_1/c$: $a = 1046.17(10)$, $b = 993.21(10)$, $c = 2167.5(2)$ pm, $\beta = 97.627(3)°$, $V = 2.2322(4)$ nm^3; $Z = 4$, $\rho_{calcd} = 1.851$ Mg m^{-3}, $\lambda = 0.71073$ pm, $T = 143$ K. A crystal (0.27 × 0.20 × 0.17 mm) was mounted in perfluoropolyether at −130 °C on a Bruker SMART 1000 CCD. Intensities were registered to $2\theta = 60°$. Of 40121 reflections, 6787 were independent ($R_{int} = 0.0524$). An absorption correction was based on multiple scans. The structure was solved by direct methods and refined against F^2 (SHELXL-97) (SHELXL-97: G. M. Sheldrick, Universität Göttingen, **1997**). Methyl H atoms were included using rigid groups, all other H atoms with a riding model. Final $wR2 = 0.0461$ based on F^2 for all data, conventional $R(F) = 0.0206$, for 283 parameters; max. $\Delta\rho = 722$ e nm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143302. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Spin Frustration in a Dimeric Mn^{II} Complex with a Metallocene-Substituted α-Nitronyl Nitroxide Radical**

Daniel Ruiz-Molina, Christian Sporer, Klaus Wurst, Peter Jaitner,* and Jaume Veciana*

The synthesis of new molecular magnetic materials that combine paramagnetic metal ions and pure organic radicals as ligating sites has attracted much more attention in the last few years.[1] Such systems enhance the diversity and/or dimensionality of magnetic systems made up from paramagnetic metal ions and diamagnetic coordinating ligands. So far, different types of stable organic radicals have been studied although one of the families most extensively used is that of α-nitronyl nitroxides (NIT). Since the nitroxyl groups are only weakly coordinating, α-nitronyl nitroxides bearing different coordinating functionalities have been reported.[2, 3] Variation of the coordination ability provided access to new complexes, whose diversity ranged from discrete molecules[4] to high-spin clusters[5] and to extended two- or three-dimensional systems.[6] Another approach successfully used to expand the dimensionality of the systems, ensuring the presence of large exchange interactions, has been the use of multicoordinating polyradical ligands. For instance, Iwamura et al. reported complexes with such polyradicals and manganese(II) hexa-

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[*] Prof. J. Veciana, Dr. D. Ruiz-Molina
Institut de Ciencia de Materials de Barcelona (CSIC)
Campus Universitari de Bellaterra 08193, Cerdanyola (Spain)
Fax: (34) 93-580-5729
E-mail: vecianaj@icmab.es

Prof. P. Jaitner, C. Sporer, Dr. K. Wurst
Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck
Innrain 52a, 6020 Innsbruck (Austria)
Fax: (43) 512-507-2934
E-mail: Peter.Jaitner@uibk.ac.at

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fluoroacetylacetonate, $[Mn(hfac)_2]$, showing two- or three-dimensional networks that exhibited ferrimagnetic behavior.[7] Herein we propose the use of the ruthenocene-substituted α-nitronyl nitroxide diradical $[Ru(NIT)_2]$ (see Scheme 1), previously reported by us,[8] as a new multicoordinating ligand to obtain complexes that combine paramagnetic metal ions and organic radicals and show nonconventional magnetic behaviors.

Complex **1** (hfac = hexafluoroacetylacetonate; IMH = reduced form of the imino nitroxide) was obtained from $[Mn(hfac)_2]\cdot 2H_2O$ and $[Ru(NIT)_2]$. During the complexation

$[\{Mn(hfac)_2\}_2\{Ru(NIT)(IMH)\}_2]\cdot 2C_7H_{16}$ **1**

reaction a partial reductionof the $[Ru(NIT)_2]$ diradical to the monoradical [Ru(NIT)(IMH)] takes place (Scheme 1). This fact was confirmed by X-ray structure analysis[9] and the IR spectrum of complex **1**, which exhibited an absorption peak at 3350 cm^{-1} characteristic of the stretching vibration of the N−H group.

The reduction of α-nitronyl nitroxide radicals in the presence of $[Mn(hfac)_2]$ has already been described.[10] In all the examples so far reported, the reduced radicals bind to the manganese ions through the O(1) atom of the amidino-oxide group to generate a dimeric structure, which seems to be the structure thermodynamically favored. This is also the case for complex **1** as shown by the ORTEP views of the $[\{Mn(hfac)_2\}(Ru(NIT)(IMH))]$ asymmetric unit and complex **1** in Figure 1.

The asymmetric unit comprises one Mn^{II} center and one [Ru(NIT)(IMH)] unit coordinated to the Mn^{II} center through the O(1) atom of the amidino-oxide group. The N(1)−O(1) bond length of 1.376(3) Å is in agreement with those reported in analogous reduced radicals, which range from 1.37 to 1.39 Å. Moreover, the substituents on the cyclopentadienyl rings adopt a *cisoid* conformation resulting from an intramolecular H(2n)$\cdots$O(4) hydrogen bond of 2.00 Å. This hydrogen bond is expected to play an active role in enhancing the magnetic exchange interactions between the Mn^{II} ions and the organic radicals. The uniqueness of the system becomes clearly apparent when the complete structure of complex **1** is considered. As shown in Figure 1, complex **1** adopts a butterfly arrangement in which the two Mn^{II} atoms occupy the central or body positions of the core and the nonreduced NIT radicals occupy the external or wing-tip positions. This type of arrangement has already been shown to induce spin frustration in polynuclear transition metal complexes consisting of four interacting metal ions.[11]

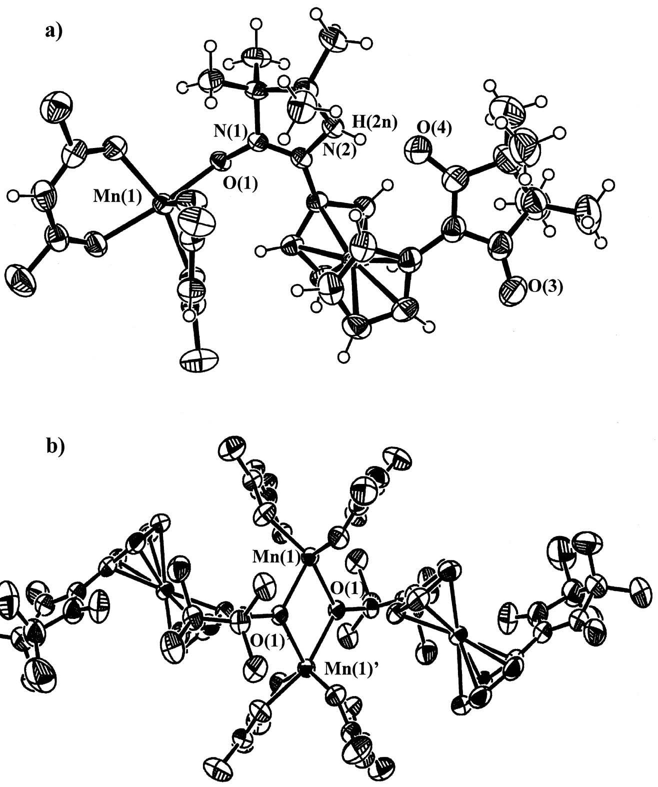
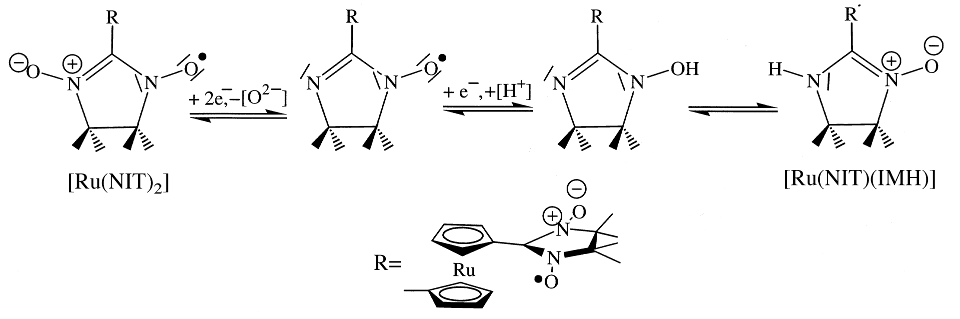


Figure 1. ORTEP views of a) the $[\{Mn(hfac)_2\}(Ru(NIT)(IMH))]$ asymmetric unit and b) complex **1**. The fluorine atoms have been omitted for clarity. The central Mn$\cdots$Mn distance is 3.546(1) Å with Mn(1)-O(1)-Mn(1)′ and Mn(1)-O(1)′-Mn(1)′ bridging angles of 108.8°. The bond lengths Mn−O(1) and Mn−O(1)′ are 2.164(2) and 2.198(2) Å, respectively.

Variable-temperature magnetic susceptibility data for a crystalline sample of complex **1** was measured on a SQUID susceptometer over the temperature range of 2–300 K with an applied external field of 1 kG. A plot of χT versus T is depicted in Figure 2. The value of χT gradually decreases from 7.8 emu K mol^{-1} at 300 K to 0.4 emu K mol^{-1} at 2 K. Attempts to fit the data in Figure 2 to the equation defined for a pair of interacting $S_1 = S_2 = 5/2$ systems with an isotropic exchange interaction and two noninteracting $S = 1/2$ radicals were unsuccessful. By contrast, the data was nicely fitted to a magnetic model based on a butterfly arrangement of the metal ions and organic radicals, consistent with the structure shown in Figure 1. The spin Hamiltonian, $\hat{H}$, for this butterfly system is given by Equation (1),[12] where J is the wing-tip/body exchange interaction between the manganese(II) ions and the organic radicals and J_{13} is the body/body interaction between the two manganese(II) ions (Scheme 2).



Scheme 1. Mechanism proposed for the partial reduction of the $[Ru(NIT)_2]$ diradical to the monoradical [Ru(NIT)(IMH)].

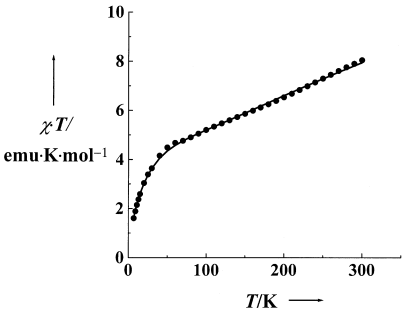
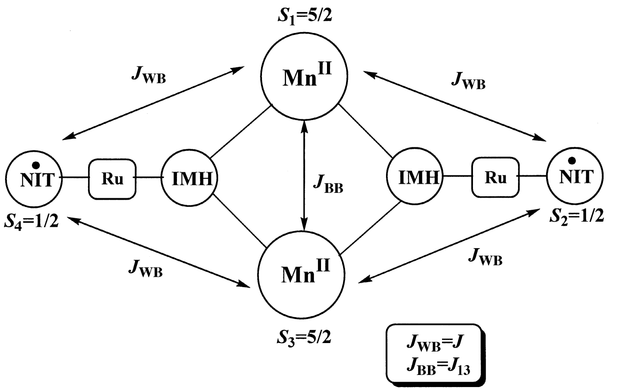


Figure 2. Temperature dependence of the magnetic susceptibilities for complex **1** in the form χT versus T. The solid line was calculated with the descibed equation and parameters.



Scheme 2. Butterfly-like arrangement of the metal ions and organic radicals in the structure of complex **1** and magnetic exchange coupling constants involved.

Equation (1) can be transformed to Equation (2) with $\hat{S}_{13} = \hat{S}_1 + \hat{S}_3$, $\hat{S}_{24} = \hat{S}_2 + \hat{S}_4$, $\hat{S}_T = \hat{S}_{13} + \hat{S}_{24}$. The eigenvalues E deduced from Equation (2) using the Kambe method[13] are shown in Equation (3), where $S_{13} = S_1 + S_3$, $S_{24} = S_2 + S_4$, and $S_T = S_{13} + S_{24}$.

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1) - 2J_{13}\hat{S}_1\hat{S}_3 \qquad (1)$$

$$\hat{H} = -2J(\hat{S}_T^2 - \hat{S}_{13}^2 - \hat{S}_{24}^2) - 2J_{13}\hat{S}_{13}^2 \qquad (2)$$

$$E = -J[S_T(S_T+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J_{13}[S_{13}(S_{13}+1)] \qquad (3)$$

A theoretical expression for the χT versus T behavior of complex **1** was derived from Equation (3) and the Van Vleck equation, and the resulting expression, modified to take into account intermolecular interactions (θ) in the molecular field approximation, was then used to least-squares fit the experimental data.[14] The best fit was obtained for $J = -31.8$ cm^{-1}, $J_{13} = -9.8$ cm^{-1}, $\theta = -6.4$ K, and $g = 1.91$. The value of the body/body interaction, $J_{13} = -9.8$ cm^{-1}, is within the range of those previously reported for the same kind of interaction in other butterfly-like tetranuclear manganese clusters, as it is also the case for the g values (1.70–2.00).[15] However, the value of $J = -31.8$ cm^{-1}, associated to the magnetic exchange coupling between the manganese(II) ions and the NIT radicals, is considerably smaller than those previously reported for other mono- and polynuclear complexes with the radicals directly coordinated to Mn^{II} ions through the O atom of the N–O group.[16] This fact is not surprising if we consider that in the latter complexes there is a direct overlap between the d orbitals of the manganese ions and the π orbitals of the radicals, whereas in the complex described herein, the exchange interaction occurs mediated by the diamagnetic IMH ligand. A plausible explanation of the magnetic exchange interactions could be that the IMH part of the [Ru(NIT)(IMH)] group promotes an antiferromagnetic exchange interaction between the Mn^{II} centers as well as an antiferromagnetic exchange between the Mn^{II} atoms and the peripheral NIT radical groups. The latter may be due either to a delocalization of spin density over the ruthenocene unit or to a spin polarization mechanism. Such a spin polarization mechanism may take place through the σ skeleton of the ruthenocene unit and, most likely, through the O-N-C-N-H group of the reduced IMH unit.[17] That both exchange coupling parameters, J and J_{13}, are negative indicates that any two neighboring spins tend to align antiferromagnetically. However, the topological arrangement of metal ions and organic radicals in the butterfly structure results in a spin frustration due to the presence of competing interactions. The ground state of complex **1** is, in the format (S_T,S_{13},S_{24}), the quintet state (2,3,1) with a first triplet excited state (1,2,1) and a second septet excited state (3,4,1) at energies above the ground state of 4 and 14 cm^{-1}, respectively. This is one the rare examples of a spin-frustrated system composed of organic radicals and metal ions. As far as we know, there is only another example described by Iwamura et al.[18] with the main difference that in the latter case the body/body interaction J_{13} corresponded to the interaction between the two radicals, which are covalently linked, whereas in the complex described herein such an interaction corresponds to the interaction between the two manganese ions.

In summary, we have shown that metallocene-substituted α-nitronyl nitroxides are good multicoordinating ligands for obtaining new complexes following the metal–radical approach. In addition, we have reported a new dimeric Mn^{II} complex with a butterfly structure and competing magnetic exchange interactions between the manganese ions and the organic radicals. Efforts are currently underway to obtain new complexes derived from [Ru(NIT)$_2$], or related metallocene diradicals, with two- or three-dimensional extended structures.

Experimental Section

1: A solution of [Mn(hfac)$_2$]·2H$_2$O (0.370 mmol) in dry *n*-heptane (20 mL) was refluxed until the solution acquired a light yellow color. After stabilization at 60 °C, a solution of diradical [Ru(NIT)$_2$] (0.185 mmol) in dry chloroform (2 mL) was added under vigorous stirring. The resulting mixture was filtered under argon and allowed to stand at room temperature for one day giving a blue precipitate. Single crystals of **1** were grown from an *n*-heptane/chloroform solution by means of a crystallization box equipped with a heating block described by Hulliger.[19]

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[9] X-ray structure analysis of $C_{68}H_{70}F_{24}Mn_2N_8O_{14}Ru_2 \cdot 2\,C_7H_{16}$, $M_r = 2191.7$; blue prism with the dimensions $0.8 \times 0.4 \times 0.3$ mm; triclinic, space group $P\bar{1}$ (no. 2), $a = 12.883(5)$, $b = 14.113(5)$, $c = 15.274(5)$ Å, $\alpha = 101.63(2)$, $\beta = 113.55(2)$, $\gamma = 91.78(2)^\circ$, $V = 2474.2(15)$ Å^3, $\rho_{calcd} = 1.471\,g\,cm^{-3}$, $Z = 1$, $T = 218(2)$ K, $\mu(Mo_{K\alpha}) = 0.71703$. Bruker P4 diffractometer, corrected for Lorentz, polarization, and absorption (ψ scans); 7937 measured reflections, of which 6747 with $I > 2\sigma(I)$ were included in the structure refinement against F^2 (SHELXL 93). The structure was solved by direct methods (SHELXS 93); heavy atoms with anisotropic temperature factors; the hydrogen atom at N(2) was found and refined isotropically; the other hydrogen atoms were calculated. Three CF_3 groups display an orientation disorder of the fluorine atoms. Refinement with 681 variables with a GOF of 1.033, $R_1 = 0.0349$ (against $|F^2|$) and $R_2 = 0.0864$ (against $|F|$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142644. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$Al_5Br_7 \cdot 5\,THF$—The First Saltlike Aluminum Subhalide

Christoph Klemp, Gregor Stößer, Ingo Krossing, and Hansgeorg Schnöckel*

In memory of Josef Goubeau

Al^{III} halides have been studied intensively in the solid state, in solution, and in the gas phase,[1, 2] whereas for aluminum subhalides for a long time only the monomeric AlX high-temperature molecules had been characterized by gas-phase IR spectroscopy.[3, 4] With the development of matrix isolation spectroscopy, subsequently dimeric Al_2X_2 species were also investigated.[4, 5] A further development of this technique for preparative applications was presented by the cocondensation technique, which provided access to a donor-stabilized metastable AlX solution.[5] From these solutions, Al^{II} and Al^{I} halides, in the form of $Al_2Br_4 \cdot 2\,anisole$ and $Al_4Br_4 \cdot 4\,NEt_3$, respectively, were structurally characterized for the first time in 1994,[6] and additional isomers of the type $Al_2X_4 \cdot 2\,D$ and $E_4X_4 \cdot 4\,D$ (D = Donor) have since been found.[7] The first polyhedral subhalide $Al_{22}X_{20} \cdot 12\,D$, which we reported on recently in this journal,[8] represented a new compound type. Herein we report on the first example for the mixed-valent compound type $Al_5X_7 \cdot 5\,D$.

Cocondensation of the high-temperature molecule AlX (X = Cl, Br, I) with a toluene/THF mixture according to the method described in reference [5] gave dark red-brown, metastable $AlX \cdot THF$/touene solutions. The AlI solution decolorized at room temperature, without the deposition of aluminum, and colorless crystals of $Al_2I_4 \cdot 2\,THF$ (**1**) were isolated after cooling of the concentrated solution.[9] Compound **1** displays the typical $D \cdot X_2Al{-}AlX_2 \cdot D$ structure.[10] In contrast, in addition to aluminum, among others, the well-known $AlCl_3 \cdot THF$[2b] precipitated from the the AlCl solution at room temperature.

Besides aluminum and $Al_{22}Br_{20} \cdot 12\,THF$[8] the $AlBr \cdot THF$/toluene solution afforded a colorless, brittle compound (**2**) of the composition "$Al_5Br_7 \cdot 5\,THF$", which crystallizes in the triclinic crystal system. An X-ray crystal structure analysis revealed that **2** is a salt comprising $[Al_5Br_8 \cdot 4\,THF]^-$ ions and $[Al_5Br_6 \cdot 6\,THF]^+$ ions (**2a** and **2b**, respectively; Figure 1).[9] The Al_5 framework of both ions consists of a central Al atom, which is tetrahedrally surrounded by four Al atoms. In the case of the (approximately S_4-symmetric) anion, these four Al atoms each bear two Br atoms and a coordinated THF molecule. In constrast, in the (approximately C_2-symmetric) cation only two $AlBr_2 \cdot THF$ groups as well as two $AlBr \cdot 2\,THF$ groups are arranged about the central Al atom. Thus the formula $[Al(AlBr \cdot 2\,THF)_2(AlBr_2 \cdot THF)_2]^+[Al(AlBr_2 \cdot THF)_4]^-$ provides a better description of the bonding situation. This ion pair possesses two Al atoms with the formal

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[*] Prof. Dr. H. Schnöckel, C. Klemp, G. Stößer, Dr. I. Krossing
Institut für Anorganische Chemie der Universität Karlsruhe (TH)
Engesserstrasse, Gebäude 30.45
76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: hg@achpc9.chemie.uni-karlsruhe.de