Synthesis of $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ *via* ion exchange in liquid ammonia—a new, versatile access to ionic fullerides

Klaus Himmel and Martin Jansen*†

Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

The ammoniate $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ is prepared from K_2C_{60} *via* cation exchange in liquid ammonia; the structure of the compound is determined by X-ray crystal structure analysis.

Since the discovery of superconductivity in K_3C_{60},[1] ionic fullerides have been in the focus of scientific interest. However, up to now research has been restricted to fullerides of alkali (including the analogous Tl^+), alkaline earth and some rare earth metals,[2] which form directly from the respective metal and fullerene during solid state reactions. Several attempts have been made to introduce other metals.[3] In most cases, however, the composition and constitution of the products could not be determined conclusively. To our knowledge, only the compounds $Na_{2+x}Hg_yC_{60}$[4] and $[Ni(C_5Me_5)_2]C_{60}\cdot CS_2$[5] have been fully characterized.

As the alkali fullerides readily dissolve in liquid ammonia,[6,7] ion exchange in this solvent using a thoroughly dried macroreticular exchange resin could offer a general approach to the synthesis of fullerides with any counterion that can be loaded onto the resin and is soluble in liquid ammonia, at the same time. Recently, we have shown this route to be suitable for the synthesis of fullerides with organic cations.[8] The preparation of the novel fulleride $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ reported here, and of isostructural $[Mn(NH_3)_6]C_{60}\cdot 6NH_3$ and $[Cd(NH_3)_6]C_{60}\cdot 6NH_3$,[9] extends the applicability of the exchange route to transition metals, and thus broadens its scope significantly.

Reacting a solution of K_2C_{60} in ammonia with an ion exchange resin loaded with Ni^{2+} yielded $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ in black shiny crystals.‡ Suitable crystals were selected in an inert oil matrix under a microscope and were used for an X-ray single crystal structure analysis.§

$[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ crystallises in a distorted rock salt type of structure (Fig. 1). Nickel hexaammine complexes occupy the octahedral sites in a fcc fulleride sublattice. Each molecule of ammonia of solvation is coordinated *via* a hydrogen bond to one ammonia in the ligand sphere of the ammine complex. This extended coordination sphere of Ni^{2+} can fit its shape flexibly to the needs of the octahedral site of the C_{60}^{2-} sublattice, at the same time fixing the fulleride anion orientationally. The thermal parameters of the fulleride (Fig. 2) are reasonable and do not indicate any disorder. The shortest intermolecular carbon to carbon distance is 3.36 Å (3.11 Å in neutral C_{60}). By comparing the shortest Ni–C distance (4.62 Å) with the distance between the centre of the octahedral site and the nearest carbon atom in fcc C_{60} (3.65 Å) it becomes evident that the accommodation of the hexaammine complex and the extra six solvent molecules per formula unit leads to a considerable expansion of the C_{60} sublattice. The quite strong deviation of the crystal structure from the ideal cubic symmetry of rock salt indicates that packing requirements more strongly determine the structure than do electrostatic interactions. Hydrogen atoms of the solvent ammonia show the shortest intermolecular distances to the fulleride. This fact suggests an interaction of N–H dipoles with electron density on the fulleride surface that could be responsible for the localisation of the anion in a fixed orientation. Similar interactions of C–H dipoles have been discussed previously.[10]

Dianions C_{60}^{2-} should be subject to Jahn–Teller distortion due to the asymmetric occupation of the degenerate t_{1u} orbital of neutral C_{60}. The nature and the degree of this distortion, however, have been discussed controversially.[11] In particular, it can be very difficult to separate distortions caused by an intrinsic Jahn–Teller effect from those due to a low site symmetry of the unit under discussion. The fulleride dianion in the present structure is somewhat distorted from the ideal I_h symmetry. The mean distance of the carbon atoms from the centre of the fulleride is 3.541(2) Å with a spread from 3.555(2) Å (C13) to 3.520(3) Å (C16). Though the range is larger than in neutral C_{60} (0.012 Å),[12] it could well be a result of the interactions with the low symmetrical environment established by the hydrogen atoms. Actually, we have shown that in an environment of higher symmetry the point symmetry I_h of a divalent fulleride can be retained.[13]

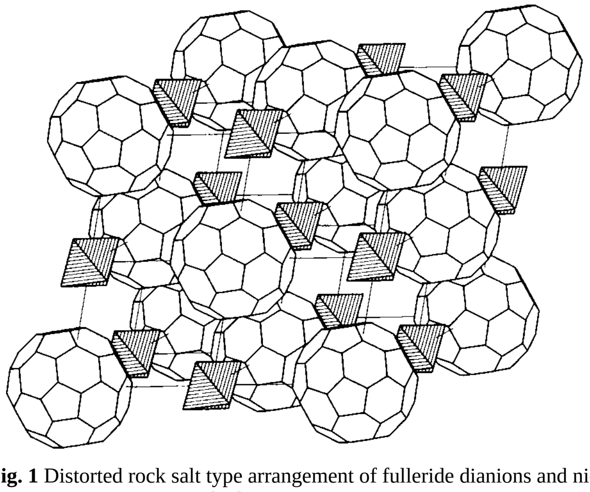

Fig. 1 Distorted rock salt type arrangement of fulleride dianions and nickel hexaammine cations (octahedra)

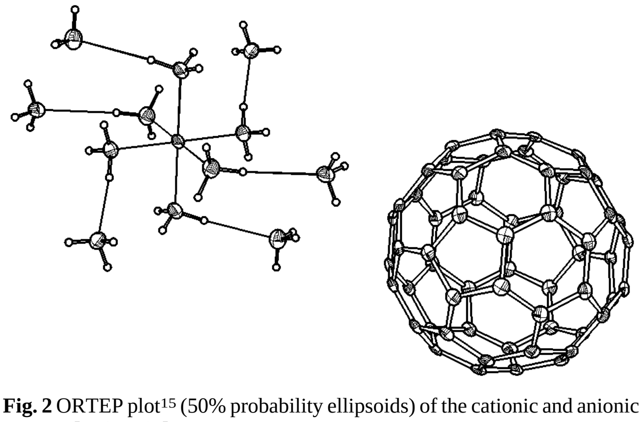

Fig. 2 ORTEP plot[15] (50% probability ellipsoids) of the cationic and anionic units in $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$

Apart from the Ni compound presented in this paper we have been able to synthesise $(BnNMe_3)_2C_{60}\cdot 3NH_3$;[8] $(PhNMe_3)_2C_{60}\cdot 4NH_3$, $[Mn(NH_3)_6]C_{60}\cdot 6NH_3$ and $[Cd(NH_3)_6]C_{60}\cdot 6NH_3$[9] *via* ion exchange in liquid ammonia, which demonstrates the wide, general applicability of the procedure developed. As an attractive option, these ammoniates offer access to fullerides of transition metals by removing ammonia *in vacuo* and/or at elevated temperatures.

We wish to thank Hoechst AG, Frankfurt, for providing C_{60}.

Notes and References

† E-mail: mjansen@snchemie2.chemie.uni-bonn.de

‡ Preparation of nickel hexaammine fulleride ammoniate: 1 g of exchange resin (Amberlyst 15, Fluka) loaded with Ni^{2+} was thoroughly dried and placed on one side of a H-type glass vessel equipped with a glass sieve (porosity 3). 80 mg (1.0×10^{-4} mol) K_2C_{60} were placed on the other side of the sieve. After cooling (ethanol–dry ice slush) ammonia was condensed into the vessel until the glass sieve was completely covered. The reaction mixture was stored at 230 K for about 3 weeks. In this time K_2C_{60} slowly diffused onto the ion exchange resin where $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$ precipitated as shiny black platelets that are sensitive to air, moisture and elevated temperature. The crystals were removed from liquid ammonia, transferred into an inert oil mixture (1 : 1 Perfluorpolyether 216, Riedel-de Haën/Perfluorpolyether Fomblin Y HVAC 40/11, Aldrich) which was cooled with a nitrogen stream to 230 K, and picked up on the tip of a glass capillary mounted on a goniometer head.

§ *Crystal data* for $[Ni(NH_3)_6]C_{60}\cdot 6NH_3$: $C_{60}H_{36}N_{12}Ni$, M = 938.72, black platelets, triclinic, space group $P\bar{1}$ (no. 2), a = 988.3(2), b = 1021.1(2), c = 1050.2(2) pm, α = 77.79(2), β = 80.04(2), γ = 79.64(2)°, $V = 1.0089(3)\ nm^3$, Z = 1, $D_c = 1.619\ g\ cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 0.55\ mm^{-1}$. 4611 reflections measured, 3959 independent, 3653 reflections observed with $I > 2\sigma(I)$, 361 parameters, no restraints. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer (Mo-Kα, λ = 71.069 pm) at 113(2) K to θ_{max} = 26°. The structure was solved by the Patterson method and refined on F^2 using all independent reflections.[14] Hydrogen atoms of the ammonia molecules were located by difference Fourier synthesis. The final wR_2 value was 0.099 [corresponding to a conventional R value of 0.037 by using only reflections with $I > 2\sigma(I)$]. CCDC 182/844.

1 (*a*) A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600; (*b*) K. Holczer, O. Klein, S.-M. Huang, R. B. Kaner, K.-J. Fu, R. L. Whetten and F. Diederich, *Science*, 1991, **252**, 1154.

2 (*a*) A. C. Duggan, J. M. Fox, P. F. Henry, S. J. Heyes, D. E. Laurie and M. J. Rosseinsky, *Chem. Commun.*, 1996, 1191; (*b*) A. R. Kortan, N. Kopylov, E. Özdas, A. P. Ramirez, R. M. Fleming and R. C. Haddon, *Chem. Phys. Lett.*, 1994, **223**, 501; (*c*) E. Özdas, A. R. Kortan, N. Kopylov, A. P. Ramirez, T. Siegrist, K. M. Rabe, H. E. Bair, S. Schuppler and P. H. Citrin, *Nature*, 1995, **375**, 126; (*d*) A. S. Ginwalla, A. L. Balch, S. M. Kauzlarich, S. H. Irons, P. Klavins and R. N. Shelton, *Chem. Mater.*, 1997, **9**, 279.

3 (*a*) Z. Gu, J. Qian, Z. Jin, X. Zhou, S. Feng, W. Zhou and X. Zhu, *Solid State Commun.*, 1992, **82**, 167; (*b*) D. K. Patel, D. M. Thompson, M. C. Baird, L. K. Thompson and K. F. Preston, *J. Organomet. Chem.*, 1997, **545–546**, 607.

4 J. M. Fox, P. F. Henry and M. J. Rosseinsky, *Chem. Commun.*, 1996, 2299.

5 W. C. Wan, X. Liu, G. M. Sweeney and W. E. Broderick, *J. Am. Chem. Soc.*, 1995, **117**, 9580.

6 D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Tully and R. E. Walstedt, *J. Phys. Chem. Solids*, 1992, **53**, 1321

7 W. K. Fullagar, P. A. Reynolds and J. W. White, *Solid State Commun.*, 1997, **104**, 23.

8 K. Himmel and M. Jansen, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1.

9 K. Himmel and M. Jansen, unpublished results. The crystal structures have been determined by single crystal X-ray diffraction.

10 P. Paul, Z. Xie, R. Bau, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 1994, **116**, 4145.

11 (*a*) N. Koga and K. Morokuma, *Chem. Phys. Lett.*, 1992, **196**, 191; (*b*) P. Bhyrappa, P. Paul, J. Stinchcombe, P. W. D. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 1993, **115**, 11 004; (*c*) M. M. Khaled, R. T. Carlin, P. C. Trulove, G. R. Eaton and S. Eaton, *J. Am. Chem. Soc.*, 1994, **116**, 3465; (*d*) P. W. D. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R. D. Bolskar, Y. Sun and C. A. Reed, *J. Am. Chem. Soc.*, 1995, **117**, 2907; (*e*) P. C. Trulove, R. T. Carlin, G. R. Eaton and S. Eaton, *J. Am. Chem. Soc.*, 1995, **117**, 6265.

12 H. B. Bürgi, E. Blanc, D. Schwarzenbach, S. Liu, Y.-J. Lu, M. M. Kappes and J. A. Ibers, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 640.

13 K. Himmel and M. Jansen, *Inorg. Chem.*, in press.

14 G. M. Sheldrick, SHELXS 86/SHELXL 93, Programs for Crystal Structure Determination and the Refinement of Structures, University of Göttingen, 1986 and 1993.

15 C. K. Johnson, ORTEP, *A Fortran Thermal Ellipsoids Program for Structure Illustrations*, Oak Ridge, Tennessee, 1965 (modified by R. Hundt, Bonn University, 1970).

Received in Basel, Switzerland, 6th March 1998; 8/01862F