latter.[11] Furthermore, its stable cyclopentadienyl analogue [Cp*Cr(O)$_2$Me] does not rearrange to [Cp*Cr(O)OMe].[12] In general, the migratory insertion of oxo ligands into metal–carbon single bonds appears to be an unfavorable process.[13] It is unlikely to be kinetically competent to explain the ready transformation of **1** into **2**.

The isolation of **2** extends the scarce tris(pyrazolyl)borate chemistry of chromium to its relatively rare +IV oxidation state. It also demonstrates that there exist facile intramolecular pathways for the oxygenation of metal–carbon σ bonds by migratory insertion of O_2. Such transformations may serve as individual steps in metal-catalyzed oxidations of organic molecules by air.

Experimental Section

All experiments were carried out under exclusion of air and moisture with inert atmosphere glove box, Schlenk, or high vacuum line techniques.

2: A solution of **1** (0.50 g, 0.91 mmol) in pentane (50 mL) was charged into a glass ampoule equipped with a Teflon stopcock. After the solution was cooled to −45 °C, the ampoule was evacuated and then filled with dry O_2. The color of the solution changed immediately from blue to red. After the solution was stirred for 0.5 h, it was allowed to warm to room temperature, whereupon it turned brown. The solvent was evaporated, and the solid residue was recrystallized from Et_2O at −30 °C to yield light brown crystals of **2** (0.254 g, 48 %). M.p. 98 °C; ^1H NMR (250 MHz, [D$_6$]benzene, 25 °C): $\delta = 17.5$ (br, 9H), 9.4 (br, 27H), 1.5 (br, 3H), −35.4 (br, 3H); IR (KBr): $\tilde{\nu} =$ 3053, 2961, 2545, 1587, 1543, 1478, 1424, 1350, 1282, 1261, 1194, 1070, 1024, 922, 866, 292, 659 cm^{-1}; UV/Vis (Et_2O): λ_{max} (ε) = 415 nm (1730); μ_{eff} (25 °C) = 2.6(1) μB; elemental analysis for $C_{30}H_{45}BCrN_6O_2$: calcd (found): C 61.64 (61.38), H 7.76 (7.02).

The in-situ IR spectroscopic monitoring of the reaction of **1** with O_2 was carried out with an Applied Systems Inc. ReactIR 1000 instrument, equipped with a DiComp probe. The probe was inserted directly into a cooled (−78 °C initially) solution of **1** in toluene (0.5 M). Spectra were acquired at 4-cm^{-1} resolution, and a background spectrum of toluene was subtracted.

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A Novel Highly Charged (+12) Anion Receptor That Encapsulates Simultaneously NO_3^- and PF_6^- Ions[**]

Ralf-Dieter Schnebeck, Eva Freisinger, and
Bernhard Lippert[*]

Recently we described a molecular triangle, [{(en)Pt(bpz)}$_3$](NO$_3$)$_6$, consisting of three (en)Pt^{II} entities (en = ethylenediamine) and three 2,2′-bipyrazine (bpz) ligands that bridge metals through N(4) and N(4′).[1] In this compound the pyrazine rings adopt a transoid arrangement and are markedly twisted. We have now found that addition of chelating metal entities, for example (en)Pd^{II}, to this compound causes rotation of a pyrazine ring about the central C(2)–C(2′) bond and coordination of the heterometal atom at the N(1) and N(1′) positions. The hexanuclear cation formed in the presence of (en)Pd^{II} has a charge of +12 and exhibits a high affinity for anions. The X-ray crystal structure of [{(en)Pt(bpz)Pd(en)}$_3$](NO$_3$)$_4$(PF$_6$)$_8$ (**1**) confirms the simultaneous encapsulation of NO_3^- and PF_6^- ions in the cavity of

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[*] Prof. Dr. B. Lippert, Dipl.-Chem. R.-D. Schnebeck,
Dipl.-Chem. E. Freisinger
Fachbereich Chemie der Universität Dortmund
Otto-Hahn-Strasse 6, D-44227 Dortmund (Germany)
Fax: (+49)231-755-3797
E-mail: lippert@pop.uni-dortmund.de

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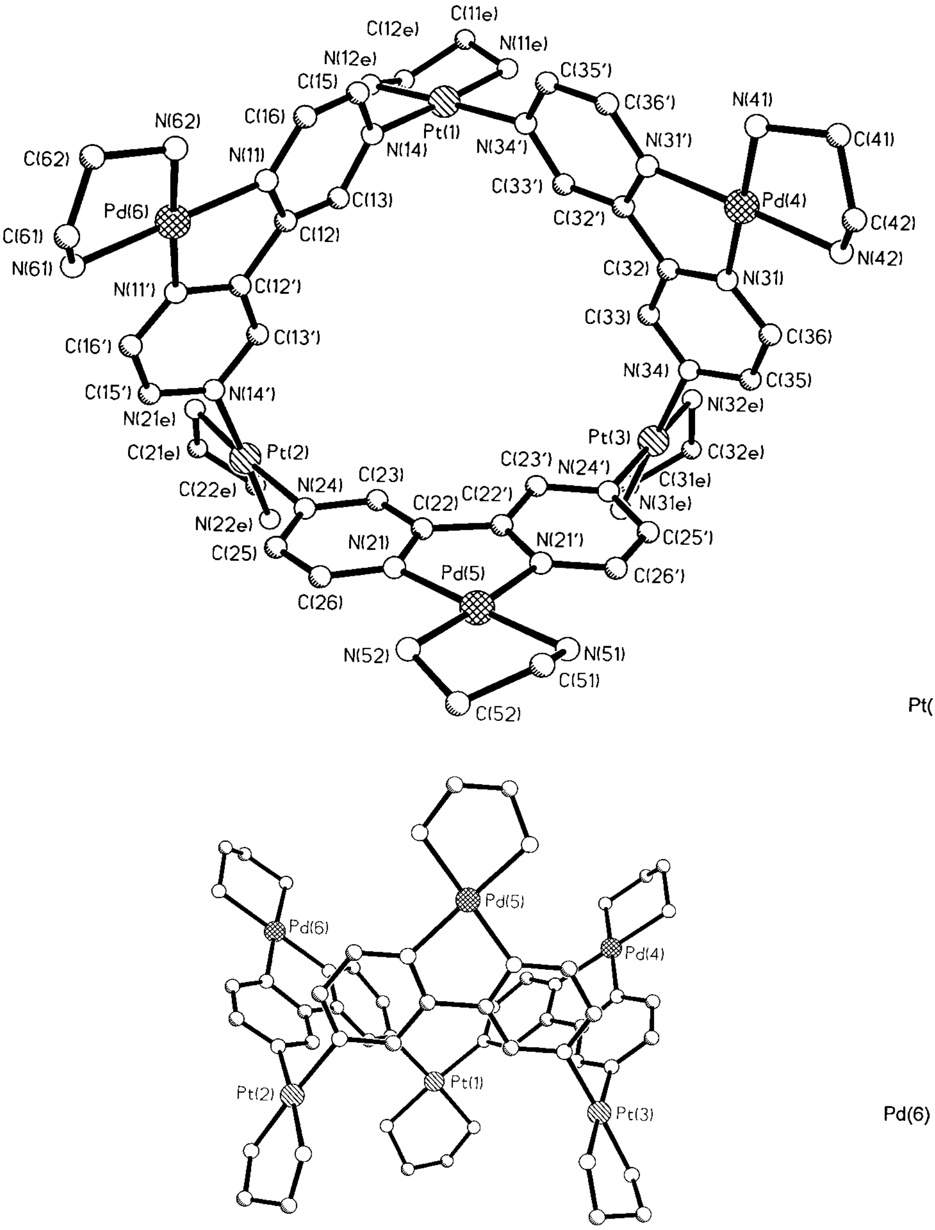

Figure 1. Top view (top) and side view (bottom) of the cation of **1**.

the cation. In solution a host–guest interaction between the cation of **1** and PF_6^- as well as other anions has been observed.

Figure 1 gives two different views of the cation of **1**.[2] The six metal atoms form the corners of a compressed, distorted trigonal antiprism. While the three Pt atoms form an equilateral triangle with side lengths of 7.88(1) Å, the Pd triangle is considerably larger and nearly isoceles (8.39(1), 8.55(1), 9.77(1) Å). The six Pt–Pd distances are about 6.82(1) Å.

The topology of the starting material [{(en)Pt(bpz)}$_3$]-$(NO_3)_6$ changes dramatically as a consequence of (en)Pd^{II} coordination (Figure 2): The molecular triangle is converted into a calixarene-like structure. The results of the X-ray crystal structure determination and NMR solution studies confirm that **1** is capable of encapsulating anions. The structure reveals that a nitrate ion is located in the center of the Pt triangle (Figure 3); the oxygen atoms of the nitrate ion point towards the Lewis acidic Pt atoms. As a consequence each Pt atom has a square-pyramidal coordination sphere (Pt–O 3.49(1), 3.26(1), 3.39(1) Å). We have observed similar Pt–O distances previously.[7] Furthermore a PF_6^- ion is located in the center of the trigonal antiprism on top of the NO_3^- ion (Figure 4). Three corners of the PF_6^- octahedron point towards the Pt atoms (Pt–F 3.87(1), 4.61(1), 4.42(1) Å), while the others are orientated towards the Pd atoms (Pd–F 3.88(1), 3.39(1), 4.31(1) Å). The distances between the oxygen atoms of the NO_3^- ion and the fluorine atoms of the PF_6^- ion are between 3.15(1) and 3.53(1) Å, with a P3–N10 distance of 4.240(8) Å. The anions are not disordered.

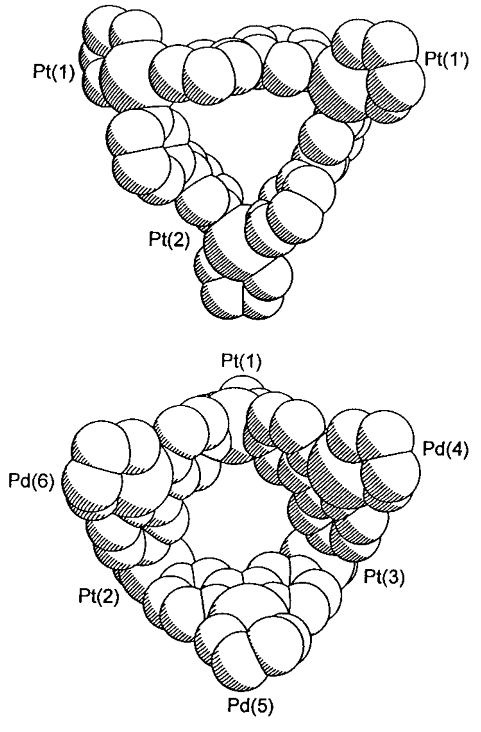

Figure 2. Space-filling models of cations of the trinuclear starting material [{(en)Pt(bpz)}$_3$]$(NO_3)_6$ (top) and of the hexanuclear product **1** (bottom).

The association constant (K_{ass})[8, 9] has been determined for PF_6^- by NMR spectroscopic investigations. The H(3) and H(3′) proton resonances are shifted by about $\Delta\delta = 0.27$ to higher field upon addition of NH_4PF_6 to the pure hexanuclear nitrate salt **1***, whereas the signals of the other aromatic protons are virtually unaffected (max. shifts $\Delta\delta = 0.03$). The ^{19}F NMR signal of NH_4PF_6, which is a doublet as a consequence of coupling between the ^{19}F and the ^{31}P nuclei, undergoes a downfield shift upon addition NH_4PF_6 to the pure nitrate salt **1***. With an excess of the PF_6^- ion, the signal shifts back to highfield. The maximum effect ($\Delta\delta = 0.36$, after addition of 4–5 equivalents of PF_6^-) is not very pronounced

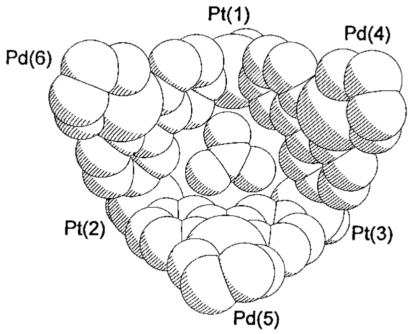

Figure 3. Space-filling model of the cation **1** with an NO_3^- ion at the bottom of the calixarene-like structure.

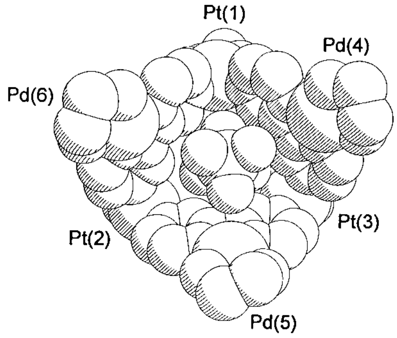

Figure 4. Space-filling model of the encapsulation of the PF_6^- ion in $[\{(en)Pt(bpz)Pd(en)\}_3(NO_3)]^{11+}$. The NO_3^- ion is omitted for clarity.

due to signal averaging between free and encapsulated anion. In the ^{31}P NMR spectrum, the septet shifts by about $\Delta\delta = 0.62$ to higher field as compared to free PF_6^- ions, after addition of one equivalent of NH_4PF_6 to **1***. A further increase in the concentration of PF_6^- ions causes the ^{31}P NMR signal to shift to the value of the free PF_6^- ion in D_2O. By analogy with the crystal structure we suggest that also in solution the PF_6^- ion is encapsulated over the Pd_3 plane. The NMR studies can, however, not confirm an encapsulation of the nitrate anion in solution.

The association constant calculated for PF_6^- from ^1H NMR data was $10.6 \pm 3.9\,\text{M}^{-1}$ (standard deviation 3σ). In comparison to other systems with host–guest interactions, this value seems to be small,[10] but it has to be taken into consideration that association constants in water are generally considerably lower than those measured in a nonpolar solvent. In water there is clearly competition between the solvent and the host. Measurements in nonpolar solvents could not be performed due to solubility problems; however, we believe that here the association constant is considerably higher.

^1H NMR experiments with other anions confirm that **1*** is also a receptor for the tetrahedral anions ClO_4^-, BF_4^-, and SO_4^{2-}. The comparison of the determined association constants (Table 1) clearly reveals that the binding of SO_4^{2-} is very strong ($255.8 \pm 57.3\,\text{M}^{-1}$). In contrast to the anions PF_6^-, ClO_4^-, and BF_4^-, H(3) and H(3′) protons are downfield shifted in the presence of SO_4^{2-}. The difference in the NMR spectra may indicate another mode of encapsulation of the SO_4^{2-} ion in **1***. One possibility would be an association over the Pt_3 plane and a replacement of NO_3^- ions. Sodium-3-(trimethylsilyl)propanesulfonate (TSP) gives no indication of any host–guest interaction. No association constants could be determined for $PtCl_4^{2-}$, $PdCl_4^{2-}$, $PtCl_6^{2-}$ and SiF_6^{2-} because of solubility problems.

Table 1. Association constants K_{ass}.

Anions	K_{ass} [M^{-1}] ± 3σ
PF_6^-	10.6 ± 3.9
ClO_4^-	9.6 ± 4.5
BF_4^-	4.1 ± 1.1
SO_4^{2-}	255.8 ± 57.3
TSP	0.0

Anion receptors are a field of great current interest.[11] Receptors for nitrate and phosphate ions are very important because of their role in enviromental pollution.[12] Among the various approaches for recognition and complexation there are also those that take advantage of electrostatic, Lewis acidic, and coordinative interactions between anionic guests and hosts containing metal entities.[13] In the present case of the simultaneous encapsulation of NO_3^- and PF_6^- ions there appears to be a combination of the first two mentioned interactions in operation. In order to find out if **1** is a sensor for these anions further experiments are necessary.

Experimental Section

1: $[(en)PdCl_2]$ (44.2 mg, 0.186 mmol) was suspended in water (10 mL) and stirred for 4 h at room temperature with $AgNO_3$ (60.1 mg, 0.354 mmol). After removal of AgCl by filtration and addition of $[\{(en)Pt(bpz)\}_3](NO_3)_6$[1] (100 mg, 0.0581 mmol) to the filtrate, the mixture was stirred for 2 h at room temperature. The orange reaction mixture was filtered and NH_4PF_6 (140 mg, 0.86 mmol) was added. Yellow-orange $\mathbf{1}\cdot 5H_2O$ was isolated in 63 % yield after 2 d at 4 °C. Satisfactory elemental analysis for $Pt_3Pd_3N_{28}C_{36}H_{76}O_{17}P_8F_{48}$; ^1H NMR (200 MHz, D_2O, TSP): $\delta = 2.96$ (s, 8H; CH_2), 8.86 (d, $^3J = 3.4$ Hz, 2H; aromatic), 9.76 (d, $^3J = 3.9$ Hz, 2H; aromatic), 10.39 (s, 2H; aromatic); ^{195}Pt NMR (43 MHz, D_2O): $\delta = -2726$ (PtN_4).

1*: The pure nitrate hexanuclear compound **1*** was prepared in an analogous manner to **1** in solution except for the addition of NH_4PF_6. Compound **1*** was identified by NMR spectroscopy: ^1H NMR (200 MHz, D_2O, TSP): $\delta = 2.97$ (s, 8H; CH_2), 8.83 (d, $^3J = 3.4$ Hz, 2H; aromatic), 9.79 (d, $^3J = 3.9$ Hz, 2H; aromatic), 10.66 (s, 2H; aromatic); ^{195}Pt NMR (43 MHz, D_2O): $\delta = -2719$ (PtN_4).

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Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101228. 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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[{Mn(salen)CN}$_n$]: The First One-Dimensional Chain with Alternating High-Spin and Low-Spin Mn^{III} Centers Exhibits Metamagnetism**

Naohide Matsumoto,* Yukinari Sunatsuki,
Hitoshi Miyasaka, Yuzo Hashimoto,
Dominique Luneau, and Jean-Pierre Tuchagues*

Of the few low-spin manganese(III) complexes,[1–3] the majority contain five or six cyano ligands.[1] Manganese(III) complexes with one or two cyano ligands are generally high spin:[4] monocyano manganese(III) porphyrins,[4a] discrete five-coordinate manganese species with L-Mn-CN coordination[4b] (L = tetradentate salen-type ligand; H_2salen = bis(salicylidene)ethylenediamine), and heterometallic species with Fe-CN-Mn(L)-NC repeat units.[4c, d] However, low-spin Mn^{III} is present in dicyanomanganese(III) porphyrins.[2] Finally, [Mn(trp)][5] (trp = tris[1-(2-azolyl)-2-azabuten-4-yl]amine) is the only manganese(III) complex known to exhibit a thermally induced $S = 1 \leftrightarrow S = 2$ spin crossover. In this complex, the ligand field generated by the three pyrrole and three imine N centers of trp is sufficiently strong to yield a Δ parameter close to the spin-pairing energy. The strong ligand field which stabilizes low-spin Mn^{III} in dicyanomanganese(III) porphyrins is probably provided by C-bonded cyano ligands in addition to the four pyrrole N donors. In this context, the question of whether the presence of two C-bonded cyanide ligands is sufficient to stabilize low-spin Mn^{III} in an octahedral coordination environment is of utmost interest. This will determine whether molecular magnetic materials can be built from a single Mn^{III} paramagnetic component.

The simplest way to obtain an NC-Mn-CN pattern is to induce CN^- bridging of $[Mn^{III}L]^+$ cations (L = planar tetradentate ligand). The reaction of an aqueous solution of NaCN with a methanolic solution of [Mn(salen)(H_2O)]ClO_4 yields red-brown microcrystals of [{Mn(salen)CN}$_n$] (**1**), a new type of one-dimensional coordination polymer which contains alternating $S = 1$ and $S = 2$ Mn^{III} spin states and exhibits

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[*] Prof. N. Matsumoto, Dr. Y. Sunatsuki, Dr. H. Miyasaka
Department of Chemistry, Faculty of Science
Kumamoto University
Kurokami 2-39-1, Kumamoto 860-8555 (Japan)
Fax: (+81) 96-342-3390
E-mail: naohide@aster.sci.kumamoto-u.ac.jp

Prof. J.-P. Tuchagues
Laboratoire de Chimie de Coordination du CNRS
UPR 8241, 205 route de Narbonne, 31077 Toulouse Cedex (France)
Fax: (+33) 561 553003
E-mail: tuchague@lcc-toulouse.fr

Prof. Y. Hashimoto
Department of Physics, Fukuoka University of Education
Akama 729, Fukuoka 811-41 (Japan)

Dr. D. Luneau
CEA-Département de Recherche Fondamentale sur la Matière Condensée
SCIB-Laboratoire de Chimie de Coordination (URA CNRS 1194)
38054 Grenoble Cédex 9 (France)

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