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Proton NMR Study of Cr−Co Heterometallic Wheel Complexes

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^{1}H NMR spectra of the paramagnetic heterometallic complexes of general formula [cation][$Cr_7CoF_8(O_2C^tBu)_{16}$] have been recorded. The NMR spectra have allowed the investigation of the structure of these complexes in solution. These experiments show that the complexes are stable and maintain the solid state structure in solution, retaining the protonated amine in the cavity of the heterometallic ring.

Introduction

High nuclearity transition metal complexes have a wide range of potential applications, from qubits in quantum computers,[1−3] to synthetic models of the active site of enzymes.[4] ^{1}H nuclear magnetic resonance (NMR) is a very useful technique in the characterization of simple coordination and organometallic complexes. However, it is rarely used to characterize paramagnetic, high nuclearity complexes.[5] In most cases this is due mainly to the difficulty in obtaining a resolvable spectrum because of fast nuclear spin relaxation caused by the paramagnetism of the compound, and also because of the complexity of the NMR spectrum of a high-nuclearity complex with a large number of inequivalent organic groups, as is the case in many polynuclear paramagnetic complexes. Paramagnetic NMR is mostly used by bioinorganic chemists[6] or in magnetic resonance imaging (MRI), a technique where paramagnetic metal complexes that are strong NMR relaxers of solvent protons are used clinically as contrast agents.[7] However, proton NMR can be a diagnostic tool to aid in structure elucidation of paramagnetic complexes if used properly, and it can have the bonus of providing information on the structure of these species in solution. One must take into account the main characteristics of paramagnetic NMR: (i) the chemical shifts will not be restricted to the 0−10 ppm scale of common proton NMR, instead, the spectral window will be as wide as 200 ppm; (ii) the proton−proton couplings will not be observed, and (iii) the peaks will be broad compared to the NMR of organic or organometallic complexes.

In 2003 Timco, Winpenny, and co-workers reported the synthesis of the first heterometallic wheel complexes [H_2NR_2][$Cr_7M^{II}F_8(O_2C^tBu)_{16}$],[8] where M^{II} = Ni, Co, Fe, Mn, Cd and R is a linear alkyl-chain. This route has been used to produce an extended family of the heterometallic rings with general formula [H_2NR_2][$M_7M^{II}F_8(O_2CR')_{16}$], where instead of the Cr(III) ion the trivalent metal M^{III} is Fe, V, Ga, In, and Al.[9] The ability to vary both metals present allows us to vary the magnetic properties of the compounds, which in the long term is important in being able to understand the magnetic phenomena seen. In particular, the Cr_7Ni(II) systems have been very carefully considered as models for double-qubit quantum gates. It has been proposed by Troiani et al.[10] that qubit gates could be designed using interactions between excited states of magnetic clusters, and recently it has been shown that two Cr_7Ni rings can be linked and their spins entangled.[11] In related work Cr_7M rings have been used as part of heterorotaxanes.[12] Future applications of these

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complexes or their derivatives would require processability, and thus their solution stability must be studied and understood. The Cr_7Co analogues of the well studied Cr_7Ni complexes were chosen for this NMR study because of the fast relaxation of cobalt(II) in an octahedral environment,[13] which would counteract the slow electronic relaxation of Cr(III) ions that usually makes NMR of Cr(III) complexes broadened beyond detection.[14,15] As reported before, the coupling between the metal centers in the wheel complexes is antiferromagnetic, and the ground state for the Cr_7Co complexes appears to be diamagnetic.[8]

In $[H_2NR_2][M_7M^{II}F_8(O_2CR')_{16}]$ complexes the cation is generally a protonated, symmetric secondary amine group, and complexes with dimethyl-, diethyl-, dipropyl-, and dioctyl-protonated amine cations, among other symmetric dialkylamines, have been synthesized and characterized with most of the heterometals.[16,17] Thus, the whole family of heteronuclear wheels comprises hundreds of members, many of these characterized by X-ray crystallography, but this single technique must be supported by other techniques to prove the true heterometallic nature of the complexes, since two different metals cannot be unambiguously distinguished by crystallography. Elemental analyses, including metal analyses, leave no doubt of the composition of the crystals, showing the expected ratio of metals for the heterometallic complexes. Mass spectroscopy confirms the heterometallic nature of the anions and that each anion only contains one divalent metal and seven trivalent metals. The combination of mass spectroscopy and elemental analysis confirm that the complexes are heterometallic, containing only one M(II) and one protonated amine. Finally, to complete the characterization of the heterometallic complexes, a technique was needed to study the structure of these species in solution. We present here a proton NMR study on the solution stability of the heterometallic wheel complexes $[cation][Cr_7Co^{II}F_8(O_2C^tBu)_{16}]$ where the cation is a protonated amine or a Na^+ ion.

Experimental Section

Unless stated otherwise, all reagents and solvents were purchased from Aldrich.

Chemicals were used without further purification. $[Co_2(H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ was prepared as previously reported.[18] The syntheses of the complexes **1**−**8** were carried out in Erlenmeyer Teflon FEP flasks supplied by Fisher. Column chromatography was carried out using Silica 60A (particle size 35−70 μm, Fisher, U.K.) as the stationary phase using a positive pressure of nitrogen, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany). The complexes $[Cr_8F_8(O_2C^tBu)_{16}]$ **1**,[19,20] $[Me_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ **2**, and $[Et_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ **3** were prepared as previously reported.[21]

$[Pr_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ 4. The compound **4** was prepared by the method given in ref 21 by using dipropylamine (Pr_2NH) instead of diethylamine (Et_2NH), and the reaction time was for 6 h at 160 °C. Compound **4** was recrystallized from a mixture of pentane/ acetone. X-ray quality crystals were grown also from a mixture of pentane/acetone. Yield (62%, based on Cr). Elemental analysis calcd (%) for $C_{86}H_{160}Co_1Cr_7F_8N_1O_{32}$: Cr 15.86, Co 2.57, C 45.01, H 7.03, N 0.61 ; found: Cr 15.77, Co 2.54, C 45.46, H 7.39, N 0.58.

ES-MS (sample dissolved in Et_2O, run in MeOH): +2294 $[M]^{+\cdot}$; +2317 $[M+Na]^+$ (100%); − 2192 $[M\text{- } Pr_2NH_2]^-$.

$[C_4H_8ONH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ 5. $CrF_3\cdot 4H_2O$ (3.0 g, 16.6 mmol), HO_2C^tBu (20 g, 196 mmol), morpholine (C_4H_8ONH) (0.60 g, 6.73 mmol), and $[Co_2(H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ (1.40 g, 1.48 mmol) were heated together at 160 °C for 43 h. The flask was cooled to room temperature (RT), and acetone (30 mL) was added with stirring. The resulting microcrystalline green precipitate was collected next day by filtration and washed with acetone. Then it was extracted in pentane (~160 mL), the solution was filtered, and the filtrate was diluted with acetone (~50 mL). Then the solution was concentrated by distillation while stirring up to ~1/4 of the initial volume. The product started to crystallize during this time. The flask was cooled to RT, and the product was filtered next day, washed with acetone, and dried in air. Yield 4.4 g (81%, based on Cr). Suitable crystals for X-ray structure characterization were obtained by slow evaporation of a solution of **5** dissolved in pentane and diluted with acetone. Elemental analysis calcd (%) for $C_{84}H_{154}Co_1Cr_7F_8N_1O_{33}$: Cr 15.96, Co 2.58, C 44.23, H 6.81, N 0.61 ; found: Cr 16.41, Co 2.70, C 44.02, H 6.81, N 0.58.

ES-MS (sample dissolved in Et_2O, run in MeOH): +2179 [M − O_2CTBu]+; +2238 [{M − $C_4H_8ONH_2$}+2Na] $^+$; +2280 $[M]^{+\cdot}$; +2303 $[M+Na]^+$ (100%); + 2368 [M+ $C_4H_8ONH_2$]$^+$; −2192 $[M - C_4H_8ONH_2]^-$.

$[C_5H_{10}NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ 6. The compound **6** was prepared by an analogous procedure to that for **5** by using piperidine ($C_5H_{10}NH$) instead of morpholine; the reaction time was 24 h, and the extraction was in diethyl ether (Et_2O). Yield 4.2 g (78%, based on Cr). X-ray quality crystals were grown from a mixture of Et_2O/acetone. Yield (62%, based on Cr). Elemental analysis calcd (%) for $C_{85}H_{156}Co_1Cr_7F_8N_1O_{32}$: Cr 15.97, Co 2.59, C 44.80, H 6.90, N 0.61 ; found: Cr 15.77, Co 2.85, C 44.36, H 6.85, N 0.58. ES-MS (sample dissolved in Et_2O, run in MeOH): +2301 $[M+Na]^+$; +2364 $[M+ C_5H_{10}NH_2]^+$ (100%); −2192 $[M - C_5H_{10}NH_2]^-$.

$[PrNH_3][Cr_7CoF_8(O_2C^tBu)_{16}]$ 7. The compound **7** was prepared by an analogous procedure to that for **5** by using 0.35 g (5.92 mmol) of propylamine ($PrNH_2$) instead of morpholine; the reaction time was 26 h at 150 °C. Yield 4.8 g (90%, based on Cr) . X-ray quality crystals were grown from a mixture of Et_2O/ acetone, (62%, based on Cr). Elemental analysis calcd (%) for $C_{83}H_{154}Co_1Cr_7F_8N_1O_{32}$: Cr 16.16, Co 2.62, C 44.25, H 6.89, N 0.62 ; found: Cr 15.74, Co 2.61, C 44.79, H 7.02, N 0.52. ES-MS (sample dissolved in Et_2O, run in MeOH): + 2393 [M+ Na-$(PrNH_2)_2$]+ (100%); −2192 $[M - PrNH_3]^-$.

$[NaCr_7CoF_8(O_2C^tBu)_{16}]$ 8. The compound **8** was initially obtained in an attempt to make compound **5**, via a reaction which had proceeded for 5 h at 140 °C. Purification by

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chromatography on a silica column afforded $[NaCr_7CoF_8(O_2C^tBu)_{16}]$ **8** from the column. Similar results were obtained passing a toluene solution of pure **5** through the silica column. A better procedure was then developed for **8**. Flash chromatography of **5** (1.5 g) on silica gel (~250 mL) using toluene as eluent afforded the product $\mathbf{8 \cdot C_6H_5CH_3}$ as the first band (in ~650 mL of eluent). No homometallic complex **1** was observed, which typically is eluted prior to any heterometallic complexes. The solvent was then evaporated under reduced pressure to give 1.35 g (yield 89%) of microcrystalline green product.

Elemental analysis calcd (%) for $C_{87}H_{152}Co_1Cr_7F_8Na_1O_{32}$: Cr 15.77, Co 2.55, Na 1.00, C 45.27, H 6.64, N 0.00 ; found: Cr 15.21, Co 2.56, Na 1.10, C 45.23, H 6.67, N 0.00 ES-MS (sample dissolved in Et_2O, run in MeOH): +2238 $[M+Na]^+$ (100%); −2192 $[M - Na]^-$.

Crystallization of **8** for single crystal structure characterization.

$\mathbf{[Na\{(H_2O)(Me_2CO)\}][Cr_7CoF_8(O_2C^tBu)_{16}]}$ **8A.** The compound $\mathbf{8 \cdot C_6H_5CH_3}$ (1.0 g) obtained by the procedure above was dissolved by refluxing and stirring in acetone (~ 45 mL). The saturated solution obtained was filtered hot and the filtrate kept at RT for 5 days. This produced a crystalline product (including X-ray quality crystals), which was filtered and washed with cold acetone. Elemental analysis calcd (%) for $C_{83}H_{152}Co_1Cr_7F_8Na_1O_{34}$: Cr 15.88, Co 2.57, Na 1.00, C 43.50, H 6.68, N 0.00 ; found: Cr 16.04, Co 2.48, Na 1.12, C 42.73, H 6.74, N 0.00 ES-MS (sample dissolved in Et_2O, run in MeOH): +2238 $[M+Na]^+$ (100%); −2192 $[M - Na]^-$.

$\mathbf{[Na\{(MeCN)(Me_2SO)\}][Cr_7CoF_8(O_2C^tBu)_{16}]}$ **8B.** The compound **8A** (0.1 g) was dissolved in Et_2O (5 mL) and $HCO_2{}^tBu$ (0.1 g), dimethyl sulfoxide (Me_2SO) (0.1 mL), $NaCO_2{}^tBu$ (0.01 g) dissolved in MeCN (5 mL) was added. The solution was stirred for 3 h, then Et_2O removed by distillation. The precipitate was collected by filtration, washed with acetonitrile, and the crude product redissolved in Et_2O (5 mL), solution filtered, then diluted with acetonitrile (5 mL) to which few drops of dimethyl sulfoxide added. Slow evaporation of the solvents to up to 1/3 of initial volume produced in 2 days a crystalline product in a quantitative yield (including X-ray quality crystals). The product was filtered, washed MeCN, and dried in air. Elemental analysis calcd. (%) $C_{82}H_{150}Co_1Cr_7F_8Na_1O_{33}S$: Cr 15.87, Co 2.57, Na 1.00, C 42.93, H 6.59, N 0.00 ; found: Cr 15.61, Co 2.46, Na 1.11, C 42.71, H 6.62, N 0.00 ES-MS (sample dissolved in Et_2O and run in MeOH): +2238 $[M+Na]^+$ (100%); −2192 $[M - Na]^-$.

Elemental analyses and mass spectroscopy (MS) were performed at the Microanalysis and MS Laboratories at the Department of Chemistry, the University of Manchester. ^1H NMR spectra were recorded in $CDCl_3$, unless said otherwise, on a Varian Gemini 300 Hz spectrometer at the Department of Chemistry, the University of Manchester. The pulse sequence used was the standard for ^1H NMR, with a non standard collection window and reduced acquisition times (ranging from 0.10 to 0.25 s depending on the sample). The spectra were collected at room temperature, each sample was locked and shimmed manually.

Structure Determinations. Data were collected on a Bruker SMART CCD diffractometer (Mo Kα, $\lambda = 0.71069$ Å). In all cases the selected crystals were mounted on the tip of a glass pin using Paratone-N oil and placed in the cold flow (100 K) produced with an Oxford Cryocooling device. Complete hemispheres of data were collected using ω-scans (0.3°, 30 s/frame). Integrated intensities were obtained with SAINT+, and they were corrected for absorption using SADABS.[22] Structure solution and refinement were performed with the SHELX-package.[23] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2. Crystal data are given in Table 1; CCDC 746229−746234.

Results and Discussion

Syntheses. The reaction of hydrated CrF_3 with $[Co_2(H_2O)(O_2C^tBu)_4(HO_2C^tBu)_4]$ in the presence of a symmetric dialkylamine in molten pivalic acid leads to the isolation of the crude product $[R_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ (R = Me, **2**; R = Et, **3**; R = Pr, **4**). The crude is then purified by column chromatography and recrystallized. Similarly, to obtain the morpholine $[C_4H_8ONH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ **5**, piperidine $[C_5H_{10}NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ **6**, and propylamine $[PrNH_3][Cr_7CoF_8(O_2C^tBu)_{16}]$ **7** derivatives hydrated CrF_3 is reacted with $[Co_2(H_2O)(O_2C^tBu)_4(O_2C^tBu)_4]$ in molten pivalic acid in the presence of the amine, but the purification process is slightly different. It was observed that upon crystallization of the product obtained after column chromatography of $[C_4H_8ONH_2][Cr_7CoF_8(O_2C^tBu)_{16}]$ **5**, the amine was not present in the crystal structure, and the complex obtained was identified as $[NaCr_7CoF_8(O_2C^tBu)_{16}]$ **8**. The small amounts of Na^+ present in the silica gel (< 0.2%, depending on the brand) can account for the Na^+ in the final product **8A**. To improve the yield of **8**, complex **8A** was recrystallized in the presence of sodium pivalate, the crystal structure of the obtained crystals **8B** showed a localized Na^+ ion in the cavity, along with a MeCN and DMSO molecules. The morpholine derivative **5** was then isolated in pure crystalline form by direct crystallization, avoiding the column chromatography step. Complexes **6** and **7** are obtained in a manner analogous to that for complex **5**, without purification by column chromatography, which also resulted in the exchange of the amine for the Na^+ and the isolation of **8A**. It appears that for these larger amines column chromatography leads to exchange of the amine with sodium.

Description of Crystal Structures. Crystal data and data collection parameters can be found in Table 1. The crystal structure of the anion of all the complexes comprises a cycle of eight metals (Figure 1a), each on a corner of an octagon, bridged by eight μ_2-F^- ions. Sixteen bridging *syn, syn*-pivalate ligands complete the octahedral coordination of all the metal centers. The pivalates can be divided in two groups, eight equatorial pivalate groups lying on the plane of the metallic wheel and eight axial pivalates, alternating their orientation up and down the plane of the wheel. In the crystal structure of complexes **2**, **3**, and **4** the cation can be found lying in the cavity of the wheel, and it is heavily disordered. There is also crystallographic disorder of the position of the Co(II) atom in the wheel. The two alkyl groups of the cation are pointing up and down of the plane defined by the metals, while the nitrogen atom of the amine is roughly in the plane. Figure 1b shows the $[Cr_7CoF_8]$ core with the cation for complexes **4**, **5**, **6**, **7**, and **8B**.

The crystal structure of complexes **5**, **6**, and **7** contain an asymmetric protonated amine cation. Essentially, the structure of the $[Cr_7CoF_8(O_2C^tBu)_{16}]^-$ anion is the same as that of complexes **2**, **3**, and **4**; there are eight equatorial pivalate groups that lie in the plane of the wheel while the eight axial pivalates alternate their orientation up and down the plane defined by the metal centers. However,

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Table 1. Crystallographic Data for Complexes **4**, **5**, **6**, **7**, **8A**, and **8B**

	4	**5**	**6**	**7**	**8A**	**8B**
cell setting, space group	monoclinic, *Cc*	monoclinic, *C*2/*c*	monoclinic, *C*2/*c*	monoclinic, *P*2(1)/*C*	monoclinic, *Cc*	monoclinic, $P12_1/n1$
temperature (K)	100 (2)	100 (2)	100 (2)	100 (2)	100 (2)	100 (2)
a (Å)	25.8867 (16)	45.120 (2)	45.1745 (11)	25.1073 (8)	13.5483 (3)	19.6702 (3)
b (Å)	20.2335 (6)	16.3843 (3)	16.3766 (4)	16.6242 (7)	29.7894 (5)	25.7942 (4)
c (Å)	25.9952 (12)	35.0977 (10)	35.1498 (7)	30.8644 (10)	30.3479 (6)	26.3871 (4)
β (deg)	110.045 (6)	114.491 (4)	114.405 (2)	110.275 (3)	100.814 (2)	92.4145 (5)
V (Å^3)	12790.9 (11)	23611.8 (13)	23680.5 (9)	12084.3 (7)	12030.8 (4)	13376.3 (4)
Z	4	8	8	4	4	4
D_x (Mg m^{-3})	1.192	1.283	1.281	1.267	1.259	1.18
radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.77	0.84	0.83	0.82	0.82	0.76
crystal form, color	prismatic, green	block, green	needle, green	block, green	plate, green	prism, green
crystal size (mm)	0.30 × 0.25 × 0.20	0.30 × 0.20 × 0.10	0.50 × 0.20 × 0.10	0.80 × 0.70 × 0.40	0.70 × 0.50 × 0.15	0.3 × 0.2 × 0.15
absorption correction	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan
$T_{\min}$	0.802	0.788	0.681	0.561	0.597	0.952
$T_{\max}$	0.861	0.921	0.921	0.736	0.886	1.061
no. of measured, independent and observed reflections	29667, 17293, 11382	54857, 23656, 15906	115634, 29349, 20883	88706, 24622, 16850	50273, 18275, 16248	144841, 16346, 9057
criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.052	0.042	0.065	0.043	0.030	0.092
$\theta_{\max}$ (deg)	25.0	26.4	28.3	26.4	25.0	22
refinement	F^2	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.096, 0.295, 1.05	0.060, 0.145, 1.01	0.092, 0.175, 1.17	0.085, 0.220, 1.05	0.058, 0.163, 1.11	0.093, 0.230, 1.15
no. of parameters	1283	1255	1265	1554	1264	1255
H-atom treatment	constrained to parent site	constrained to parent site	constrained to parent site	constrained to parent site	constrained to parent site	constrained to parent site
weighting scheme	calculated $w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 89.644P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 225.0936P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.081P)^2 + 58.8417P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 48.7616P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.070P)^2 + 53.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.014	0.002	0.001	0.001	0.002	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.87, −0.89	1.38, −0.75	1.52, −0.78	1.45, −0.82	1.45, −0.52	1.33, −0.86

there is a marked difference between the two sides of the complex. In one side of the wheel, the cavity formed by the *tert*-butyl groups of the pivalate ligands is occupied by the amine (morpholine **5**, piperidine **6** or propylamine **7**), while the other side is empty. This causes the *tert*-butyl groups of the pivalate ligands to close in on the empty side, and to slightly open-up on the occupied side. Additionally, in the crystal structure of complexes **5** and **6**, the Co(II) site in the heterometallic wheel complex has been localized without ambiguity.

Finally, the crystal structure of complex **8A** and **8B** shows a $[Cr_7CoF_8(O_2C^tBu)_{16}]^-$ anion that is isostructural to that of complexes **2**, **3**, and **4**. In **8A** the anion is bound to a sodium cation that is disordered over three sites, while in **8B** the sodium cation is localized on one edge of the octagon (Figure 1b).

Proton NMR Studies. For a neutral, homometallic wheel of ideal D_{4d} symmetry, in the proton NMR we expect to observe two peaks in a 1:1 ratio. One heterometal in the wheel, with a symmetric protonated dialkylamine in the cavity will break the symmetry among the pivalate groups and split the two expected peaks (one for the equatorial and one for the axial pivalates) into eight, as shown in Scheme 1, making proton NMR a diagnostic tool for this type of complex. New complexes with asymmetric amines have been synthesized and are reported here. In this new case, the axial pivalates oriented up and down are no longer equivalent; thus twelve peaks are expected in the NMR: four peaks integrating two *tert*-butyl groups for the equatorial pivalates, four for the axial pivalates pointing up integrating one *tert*-butyl group each, and four for the axial pivalates pointing down integrating one *tert*-butyl group each. Additionally, proton NMR has the added bonus that the proton on the protonated amine might be observed in an NMR experiment, and its chemical shift will provide us with information on the spin-density distribution in the complexes. As a reference, the ^{1}H NMR of $[Cr_8F_8(O_2C^tBu)_{16}]$ **1** was measured in $CDCl_3$. As expected, the very slow relaxation of Cr(III) made the NMR peaks very broad, and the two different types of carboxylates, axial and equatorial, could not be observed; instead, an extremely broad peak

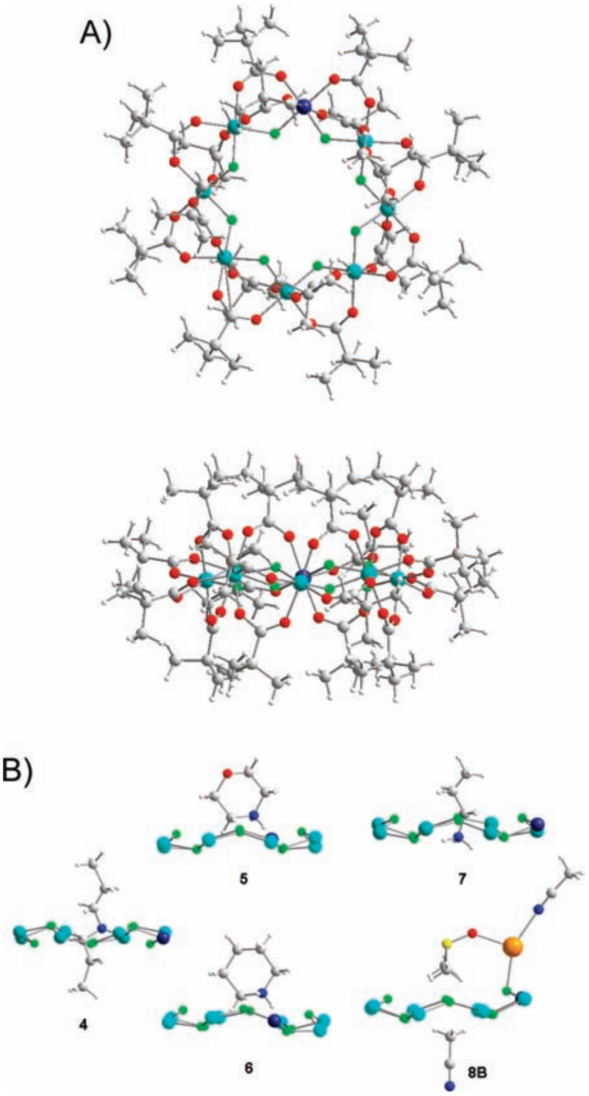


Figure 1. (a) Top view of the crystal structure of the anion $[Cr_7CoF_8(O_2C^tBu)_{16}]^-$, (b) side view of the metal-fluoride core with the cation of complexes **4**, **5**, **6**, **7**, and **8B**. Cr(III) in cyan, Co(II) in dark blue, fluoride in green, oxygen in red, carbon in gray, hydrogen in light gray, nitrogen in blue, sodium in orange, sulfur in yellow. For complexes **4**, **7**, and **8B** the Co(II) ion is not localized in one position in the crystal structure. For complexes **4** and **7** the protonated amine groups are disordered in two positions and only one is depicted for clarity.

Table 2. Proton NMR Data for Complexes **2**, **3**, **4**, and **8** in $CDCl_3$

peaks (ppm)								
2	int.	**3**	int.	**4**	int.	**8**	int	group
9.8	2	10.5	2	10.5	2	9.5	2	pivalates[a]
2.9	2	4.1	2	4.0	2	5.2	2	
2.5	2	2.6	4	2.9	2	2.3	2	
2.2	2			2.3	2	0.8	2	
1.3	2	1.2	2	1.2	2	0.3	2	
0.5	2	0.3	2	0.3	2	0.0	4	
−1.7	2	−1.5	2	0.0	2	−1.3	2	
−2.9	2	−2.6	2	−1.5	2			
						−9.5		$[H_2O-H]^+$
				−12.5				γ^b
−22.9		−19 to −22		−21 to −23				α^b
		−29.5		−33.1				β^b
				−37.2				
∼−75		∼−77		∼-80				H^+

[a] Integrals given as number of pivalate groups. [b] Position in the linear alkyl chain: N−Cα−Cβ−Cγ, etc.

Table 3. Proton NMR Data for Complexes **5**, **6**, and **7** in $CDCl_3$

peaks (ppm)						
5	int.	**6**	int.	**7**	int.	group
11.38	2	11.41	2	11.17	1	pivalates [a]
6.39	1	11.16		10.84	1	
5.30	1	7.88	1	9.46	1	
4.84	1	5.11	1	3.99	1	
3.26	1	3.47	1	3.01	1	
2.84	2	2.99	2	2.32	1	
2.05	1	1.93	2	1.73	1	
0.33	5	0.68	1	0.82	6	
0.00		0.01	4	0.48		
−1.71	1	−0.25		0.21		
−2.14	1	−0.42		−1.08	1	
		−0.68		−1.51	1	
		−1.61	1	−2.79	1	
		−1.98	1			
−15.20	CH_2	−9.57	CH_2	−12.57	CH_3	protonated amine
−17.26		−15.78	CH_2	−20/-25	CH_2	
−27.13	CH_2	−17.83		−39.36	CH_2	
−29.23		−21.62	CH_2			
∼−107	NH_2	∼−103	NH_2	∼-94	NH_2	

[a] Integrals given as number of pivalate groups.

between −1 and 4 ppm was seen in the spectrum, comprising the 16 carboxylates. The protons in the pivalate groups are separated from the metal centers by five bonds (see Scheme 2); therefore, their peaks in the NMR spectrum are sharp enough to be observed, even in complex **1**. The attempt to study the proton NMR of Cr_7Ni derivatives was unsuccessful, since the chemical shifts of the inequivalent pivalate groups were too similar and the peaks too broad. The NMR study is restricted to the Cr_7Co derivatives, and the NMR data for complexes **2**−**8** is summarized in Tables 2 and 3.

The proton NMR of complexes **2**, **3**, **4**, and **8** are shown in Figure 2. The NMR spectra show two distinct regions that will be analyzed separately. Between −5 and 15 ppm strong, sharp peaks, common to all the measured samples were observed (Figure 3). These peaks can be assigned to the pivalate groups. This was confirmed by the proton NMR spectrum of the deuterated complex $[Me_2NH_2][Cr_7CoF_8(O_2CC(CD_3)_3)_{16}]$, which showed only the peaks further upfield from −5 ppm, which are thus assigned unambiguously to the protonated amine. Because of the lower, ideal C_2 symmetry when there is one heterometal in the wheel, eight peaks are expected, as shown in Scheme 1, four correspond to the four equatorial types of pivalate (A, B, C, and D) and four to the corresponding axial carboxylates (A′, B′, C′, and D′). A close look at the pivalate region shows eight peaks for **2** and **4**, proving the presence of one Co(II) in the wheel. Even though integration is not as reliable in paramagnetic NMR as it is in NMR of diamagnetic samples, the integrals of the peaks are all of the same order, suggesting that they all correspond to the same number of protons, with each peak corresponding to 18 protons from two equivalent pivalate groups. For complexes **3** and **8**, there is some accidental overlap in the congested pivalate region; the NMR spectrum of complex **3** (Figure 2 (b)) shows seven peaks, with

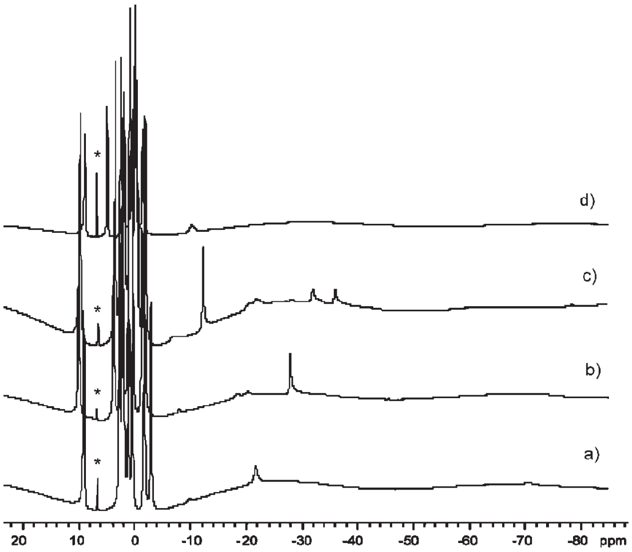
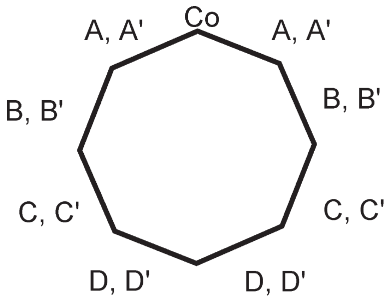
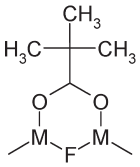


Figure 2. Proton NMR in $CDCl_3$ of: (a) **2**; (b) **3**; (c) **4**; (d) **8**. The protio-impurity of the solvent is marked with an asterisk.

Scheme 1



Scheme 2



the peak at 2.6 ppm integrating twice as much as the other six, indicating that it corresponds to two groups of pivalate ligands. This is most likely due to accidental overlap. Furthermore, some free amine can be observed in the NMR spectrum of complex **4**, as sharp peaks in the 0 to 4 ppm region.

For the cations, we expect an increasing number of peaks when going from dimethyl to diethyl to dipropyl protonated amine. From −5 to −90 ppm the broad resonances corresponding to the cations can be found. It is known that the protonated amine sits in the cavity in the solid state, but it was not obvious that this would be the case in solution. The peaks are broad and shifted all the way down to −80 ppm; this fact leaves no doubt that the amine is in close proximity to the paramagnetic metal centers in solution. Thus, in solution the protonated amine remains most of the time in the cavity of the wheel as seen in the crystal structure. In all the crystal structures obtained so far of complexes of this type, the two alkyl groups of the symmetric protonated amine seem to be equivalent, one up and one down from the plane of the wheel. This means that in the NMR we expect one peak from the Me groups in complex **2**, three peaks for the ethyl groups of **3**, and five peaks for the propyl chains of **4** (the CH_2 protons in both ethyl and propyl groups are diastereotopic and should be split in two peaks, giving thus the three peaks for an ethyl group and five for a propyl chain). The NMR spectrum of complex **2** shows two peaks in this region: a very broad small peak at ∼−78 ppm and a larger peak at −24 ppm. In some samples, a third peak at −10 ppm is also observed; this peak is very small and if a new, freshly opened $CDCl_3$ bottle is used, it does not appear. The resonance at −24 ppm is assigned to the Me groups of the cation.

The spectrum of **3** shows three peaks, the peak in the −20 ppm region is now split in two and a new peak can be seen at −30 ppm. These peaks are assigned to the CH_2 groups and the Me groups of the ethyl chains, respectively. Additionally, there is a very broad peak around −80 ppm, and as it happened in the NMR spectra of different samples of complex **2**, a resonance is sometimes observed around −10 ppm. The assignment of the peaks corresponding to the protons of the alkyl chains is supported by the T_1 time measurements, which are 0.0026 s for the two peaks between −19 and −21 ppm and 0.0037s for the peak at −29.28, the longer T_1 time indicating a longer distance between the nuclei and the unpaired electrons. Accordingly, the peak in the −30 ppm region should be split in the spectrum of complex **4**. In fact, that is what we observed, along with the appearance of a new sharper peak at −13 ppm, assigned to the Me groups of the propyl chains of the cation. The spectrum of complex **4** also shows the broad resonance around −80 ppm, as well as the appearance of a broad, small peak around −10 ppm. The very broadened peak around −80 ppm, common to the spectra of all the samples, has to be assigned to the protons bound to the neutral amine. Typical N−F distances in these complexes are between 2.7 and 3.1 Å because of N−H--F interactions, which explains the strong influence of the paramagnetic metals in the chemical shift of this proton.

The proton NMR of **8A** was investigated and confirmed the absence of protonated amine as a cation. As shown in Figure 3, the spectrum shows eight peaks between −15 and 15 ppm. Seven of these peaks are exactly in the same region as the pivalate peaks in the NMR of complexes **2**, **3**, and **4**. Furthermore, one of the peaks integrates approximately twice the amount the other six, indicating it corresponds to two peaks accidentally overlapping. These seven peaks correspond to the eight types of carboxylate groups in a heterometallic wheel with one Co(II) and seven Cr(III) ions, establishing the heterometallic nature of complex **8A**. A smaller peak is seen in the spectrum in the −10 ppm region, and it integrates for approximately two or three protons and was assigned to the water bound to the Na^+ cation in the case of **8A**. It has not been possible to clearly observe any resonance around the −80 ppm region for complex **8**. The proton NMR spectrum of complex **8B** is the same as that of **8A**, with the additional peaks of free MeCN and DMSO. As stated above a similar peak is present in the spectra of complexes **2**, **3**, and **4** at around −10 ppm, and depends greatly on the

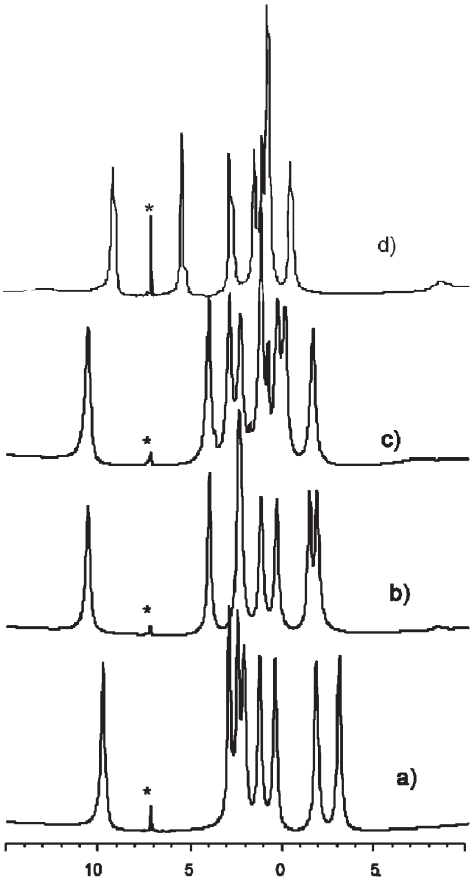


Figure 3. Downfield region of the proton NMR spectrum of complexes **2** (a), **3** (b), **4** (c), and **8** (d) showing the resonances corresponding to the eight different types of pivalate ligands. The protio-impurity of the solvent is marked with an asterisk.

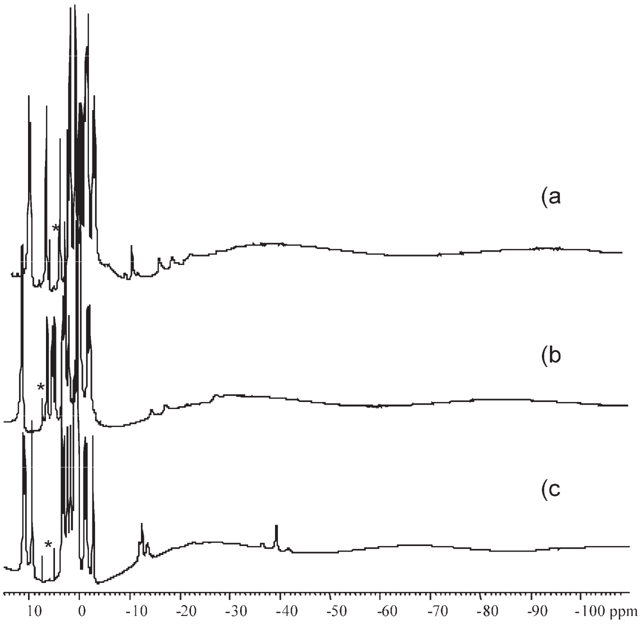


Figure 4. Proton NMR in $CDCl_3$ of (a) **5**; (b) **6**; (c) **7**. The protio-impurity of the solvent is marked with an asterisk.

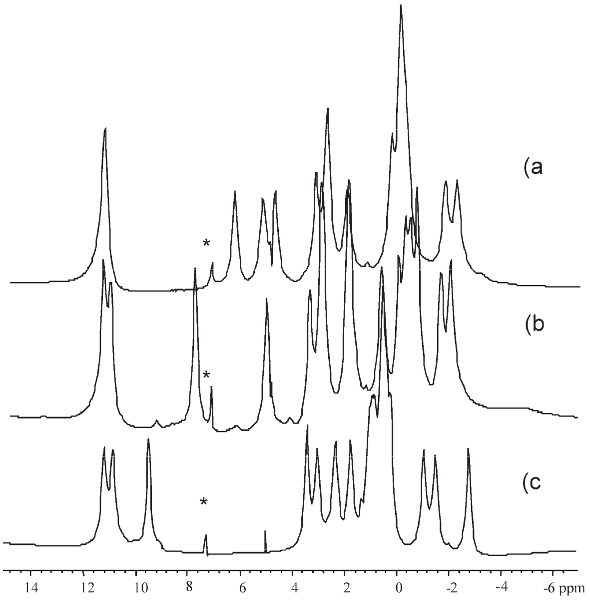


Figure 5. Downfield region of the proton NMR spectrum of (a) **5**; (b) **6**; (c) **7**, which shows the resonances corresponding to the twelve different types of pivalate ligands. The protio-impurity of the solvent is marked with an asterisk.

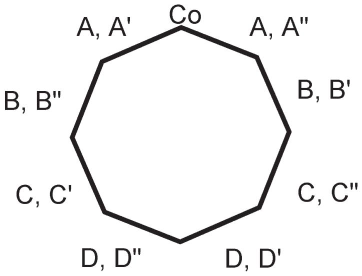
amount of water from the solvent used in the NMR. As an example, in spectra measured in freshly opened CD_2Cl_2 or $CDCl_3$, which contains very little amount of adventitious water, the peak is very small or not observed at all. It is reasonable then to assign this peak to water rapidly exchanging with the neutral amine while the complex is in solution.

Cation Exchange Experiments. Amine exchange experiments with free diethylamine and free dipropylamine were performed within an NMR tube. Also, exchange experiments with D_2O were performed. As the heteronuclear wheel complex is in solution, the ammonium cation could exchange freely with adventitious water from the solvent, generating $(H_3O)[Cr_7CoF_8(^tBuCO_2)_{16}]$ and free amine:

$$[R_2NH_2][Cr_7CoF_8(O_2C^tBu)_{16}]+H_2O \leftrightarrows (H_3O)[Cr_7CoF_8(O_2C^tBu)_{16}]+R_2NH \qquad (1)$$

When a sample of complex **3**, with a protonated diethylamine cation, was treated with free diethylamine the only change observed in the spectrum was the disappearance of the peak at ~ -10 ppm. Normally the equilibrium of eq 1 is shifted to the left, as evidenced by the absence of large NMR signals of the free amine. The addition of diethylamine should shift the equilibrium still further to the left, thus the peak at ~ -10 ppm, because of the proton in the salt $(H_3O)[Cr_7CoF_8(O_2C^tBu)_{16}]$, should disappear entirely, as observed. These observations also indicate that in the apolar solvent the complex is always neutral, the proton remains in the cavity, held in place by short contacts with the fluoride bridges, but the amine is in exchange in solution. To see if the amine could be exchanged for a different one, free diethylamine was added to solutions of complexes **2** and **8**. The results show the conversion of **2** and **8** into **3** because of the excess of diethylamine. Dipropylamine was added to a solution of complex **2**, and the same effect was now observed, the dipropylamine replaced dimethylamine in the cavity.

Scheme 3



Thus, a general equilibrium can be written for these complexes in solution:

$$[HC][Cr_7CoF_8(O_2C^tBu)_{16}]+C' \leftrightarrows [HC'][Cr_7CoF_8(O_2C^tBu)_{16}]+C$$

where C and C′ are either H_2O or a secondary linear amine. Finally, exchange with D_2O was studied. Exchange experiments of complex **8** with D_2O in $CDCl_3$ showed the broadening of the resonance assigned to the water in the cavity, at ∼−10 ppm. The same experiment performed in deuterated acetone, which permitted the use of a higher excess of D_2O, showed the disappearance of the peak at ∼−10 ppm before the fast decomposition of the sample.

The NMR spectra of the wheel complexes with nonsymmetric protonated amines as cations were also studied. These spectra are shown in Figures 4 and 5. The complexity of the spectrum is now greater because of the lower ideal symmetry of the complex, which is now C_s. Scheme 3 shows the equivalence of the different pivalate groups, in this scheme the X′ represents the axial pivalate groups pointing up and X″ the axial pivalate groups pointing down. Twelve peaks corresponding to the pivalate groups are thus expected, the four signals corresponding to the equatorial groups should integrate for two pivalate groups, while the eight signals of the axial pivalates should correspond to one pivalate group each. In fact, this is what we observe in the proton NMR spectra of complexes **5**, **6**, and **7**, confirming that the solid state structure is maintained in solution.

Conclusions

A detailed study of the structure in solution of the heterometallic paramagnetic wheel complexes of general formula [cation]$[Cr_7CoF_8(O_2C^tBu)_{16}]$ has been performed. The proton NMR confirms that the anionic complex is stable in solution. The cation is generally a protonated secondary amine, and in the crystal structure it sits into the cavity within the octanuclear wheel complex. The proton NMR clearly shows that the solid state structure is maintained in solution and that the cation is most of the time in the cavity. This stability makes this type of complexes amenable to nanostructuration and deposition on surfaces.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.