DOI: 10.1002/chem.200501497

Synthesis and Characterization of Metal-Centered, Six-Membered, Mixed-Valent, Heterometallic Wheels of Iron, Manganese, and Indium**

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Dedicated to Professor Helmut Hartung on the occasion of his 70th birthday

Abstract: Heptanuclear metal-centered, six-membered, mixed-valent, heterometallic wheels **1**–**3** of iron, manganese, and indium were prepared in a one-pot reaction from *N*-benzyldiethanolamine (H_2L^1), cesium carbonate, $[PPh_4]_2[MnCl_4]$, and $FeCl_3$ or $InCl_3$. All three complexes were characterized by the combination of elemental analysis, FAB mass spectroscopy, X-ray diffraction and cyclic voltammetry. and in the case of **1** additionally by Mössbauer spectroscopy. In **1**, four Mn^{II} ions in the periphery are arranged in pairs alternating with one Fe^{III} ion each, with an Fe^{III} ion located in the center. In **2**, three Mn^{II} ions alternate with three In^{III} ions, whereas in **3**, four In^{III} ions are arranged in pairs and alternate with one Mn^{II} ion each. In **2** and **3** an Mn^{II} ion is encapsulated in the center.

Keywords: cyclic voltammetry · heterometallic complexes · indium · iron · manganese · mixed-valent compounds · Moessbauer spectroscopy

Introduction

After the discovery of single-molecule magnets (SMMs),[1] synthetic chemists met the challenge to develop new high-spin oligonuclear transition-metal complexes. As a result, numerous homonuclear metallic wheels have been reported.[2] However, the chemistry of heterometallic wheels is still in its infancy. So far only carboxylate ligand systems are known to form heterometallic wheels,[3] but recent theoretical studies suggest that heterometallic wheels may show interesting quantum-coherence phenomena.[4] Since homometallic complexes containing N-substituted diethanolamine ligands have been the main source for new SMMs,[5] it is therefore desirable to develop a method for the synthesis of heterometallic N-substituted diethanolamine complexes of various nuclearities and structural motifs.

Previously, we reported on the synthesis of the anionic and neutral mixed-valent manganese wheels $\{Mn^{II}\subset[Mn^{II}_3Mn^{III}_3Cl_6(L^1)_6]\}^-$ ($H_2L^1 = N$-benzyldiethanolamine) and $\{Mn^{II}\subset[Mn^{II}_2Mn^{III}_4Cl_6(L^2)_6]\}$ ($H_2L^2 = N$-*n*-butyldiethanolamine), respectively.[6,7] We also observed that the neutral $\{Mn_7\}$ is ferromagnetically coupled, resulting in a high-spin ground state, and exhibits SMM behavior as well as quantum tunneling of the magnetization.[7] This exciting result prompted us to generate new mixed-valent, metal-centered, heptanuclear, six-membered heterometallic anionic and neutral wheels, containing paramagnetic Fe^{III} or diamagnetic In^{III} in addition to Mn^{II} ions. Herein, we report the successful construction and characterization of the heterometallic wheels $[PPh_4]\{Fe^{III}\subset[Fe^{III}_2Mn^{II}_4Cl_6(L^1)_6]\}$ (**1**), $[PPh_4]\{Mn^{II}\subset[Mn^{II}_3In^{III}_3Cl_6(L^1)_6]\}$ (**2**), and $\{Mn^{II}\subset[Mn^{II}_2In^{III}_4Cl_6(L^1)_6]\}$ (**3**).

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[**] Chelate Complexes, Part 32. Part 31: R. W. Saalfrank, C. Schmidt, H. Maid, F. Hampel, W. Bauer, A. Scheurer, *Angew. Chem.* **2006**, *118*, 322–325; *Angew. Chem. Int. Ed.* **2006**, *45*, 315–318.

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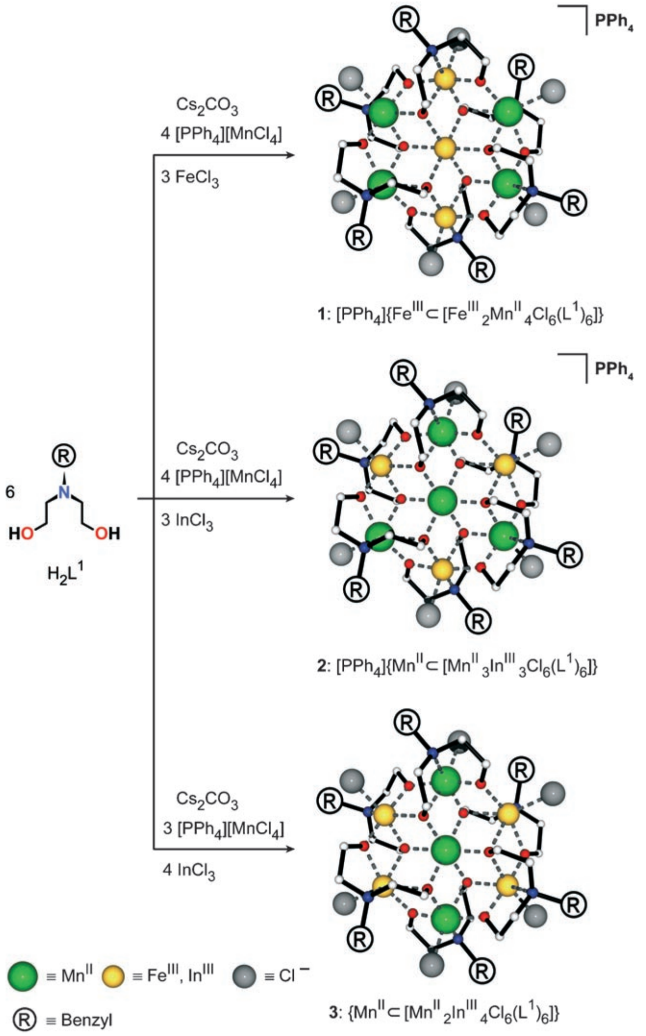
Results and Discussion

The heterometallic wheels **1**–**3** can be prepared conveniently in a straightforward one-pot reaction (Scheme 1). For this purpose, *N*-benzyldiethanolamine (H_2L^1) was deprotonated with cesium carbonate in acetonitrile at room temperature. Subsequent addition of a clear solution of a mixture of four equivalents of $[PPh_4]_2[MnCl_4]$ and three equivalents of $FeCl_3$ in CH_3CN resulted in a pale-yellow reaction mixture, which changed to brown-yellow while being stirred for seven days. Filtration of this mixture and further workup of the filtrate afforded the anionic wheel **1** in a moderate yield. The anionic indium–manganese wheel **2** was obtained similarly, only by replacing $FeCl_3$ with $InCl_3$. On the other hand, the neutral indium–manganese wheel **3** resulted from the addition of a solution of a 3:4 mixture of $[PPh_4]_2[MnCl_4]$ and $InCl_3$ in acetonitrile to the deprotonated ligand and followed by workup of the resulting violet-gray suspension. In all cases one has to follow carefully the procedures given in the Experimental Section.



Scheme 1. Synthesis of heterometallic wheels **1**–**3**.

All three complexes were characterized by elemental analysis, FAB mass spectrometry, cyclic voltammetry, single-crystal X-ray diffraction and in the case of **1** Mössbauer spectroscopy. In the solid state under N_2 at ambient temperature, **1**–**3** are stable for prolonged periods of time, while they decompose at around 200 °C. All these compounds are soluble in THF, CH_2Cl_2, $CHCl_3$, and DMF. The mass spectra indicated that the anionic wheels **1** and **2** remained unchanged even in solution for more than two weeks. However, the neutral wheel **3** decomposed partially in solution after two weeks, resulting in the formation of an all-indium wheel $[In^{III}{}_6Cl_6(L^1)_6]$, as identified by mass spectrometry. Therefore, due to the long time necessary for growing crystals suitable for X-ray analysis, instead of pure **3**, inevitably only pink-gray crystals composed of {54 % **3**·46 % $[In^{III}{}_6Cl_6(L^1)_6]$}·3.5 CH_2Cl_2 could be isolated.

The molecular structures of **1**–**3** were determined by low-temperature X-ray crystal structure analyses.[8–11] In principle, the anionic wheels **1** and **2**, and the neutral wheel **3** show the same structure. Both **1** and **2** crystallize in the triclinic space group $P\bar{1}$, with the unit cells consisting of two independent molecules situated on crystallographic inversion centers. Due to the high molecular symmetry of **1**, the X-ray structure does not allow us to distinguish between Fe^{III} and Mn^{II} sites. However, the location of the metal ions given for **1** is in accordance with the results obtained from cyclic voltammetry and Mössbauer spectroscopy, which in turn resulted in the best refinement values. The $\{Fe^{III}\subset[Fe^{III}{}_2Mn^{II}{}_4Cl_6(L^1)_6]\}^-$ ion ($\mathbf{1}^-$) is a Fe^{III}-centered wheel and consists of two Fe^{III} and four Mn^{II} ions located in the corners of a regular hexagon (Figure 1); tetraphenylphosphonium is the counterion.

The $\mathbf{1}^-$ ion possesses a crystallographically imposed inversion symmetry. Each peripheral iron and manganese atom

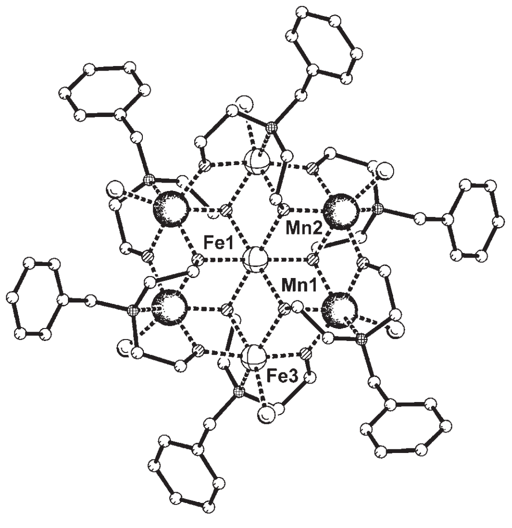


Figure 1. Pluton presentation of the molecular structure of $\mathbf{1}^-$ with the numbering of the metal centers. Mn: dots, Fe: cross, C: shade, N: net, O: diagonal, Cl: segment. H atoms and solvent molecules omitted for clarity.

exhibits a distorted octahedral coordination geometry composed of one nitrogen, one chloride, two μ_2-, and two μ_3-oxygen donors. The doubly deprotonated $(L^1)^{2-}$ ligands act as tridentate clamps, which link one Fe^{III} and two Mn^{II} in the periphery each through μ_2- and μ_3-oxygen atoms. In other words, the three Fe^{III} ions are located along the diameter of the wheel, and in the periphery pairs of Mn^{II} ions alternate with Fe^{III} ions. The central Fe^{III} ion has a distorted octahedral coordination with respect to the six inner μ_3-O donors (Fe1–O distances: 2.203(4)–2.213(5) Å).

When the mass spectrum of $[PPh_4]\{Fe^{III}\subset[Fe^{III}_2Mn^{II}_4Cl_6(L^1)_6]\}$ (**1**) is compared with its all-manganese counterpart $[NEt_4]\{Mn^{II}\subset[Mn^{III}_3Mn^{II}_3Cl_6(L^1)_6]\}$,[6] the peaks of **1** increase distinctly by three units with respect to the corresponding peaks of the all-manganese wheel. However, the isotopic distribution for Fe and Mn differs slightly (Figure 2).

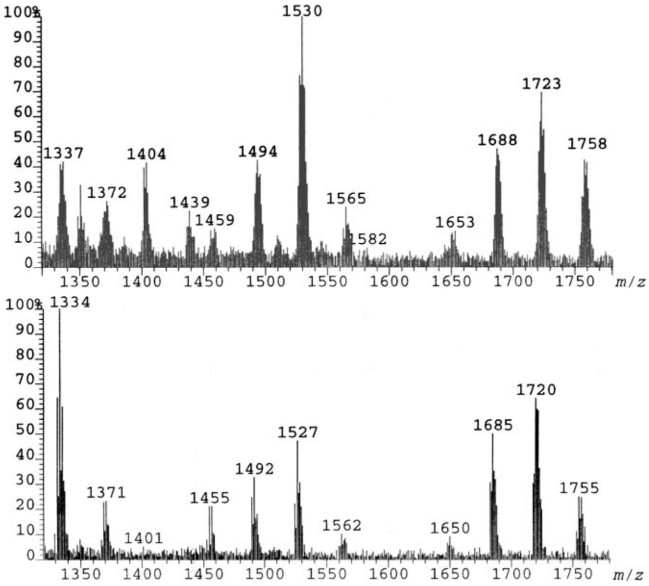


Figure 2. FAB-mass spectra of **1** (top) and $[NEt_4]\{Mn^{II}\subset[Mn^{III}_3Mn^{II}_3Cl_6(L^1)_6]\}$ (bottom).

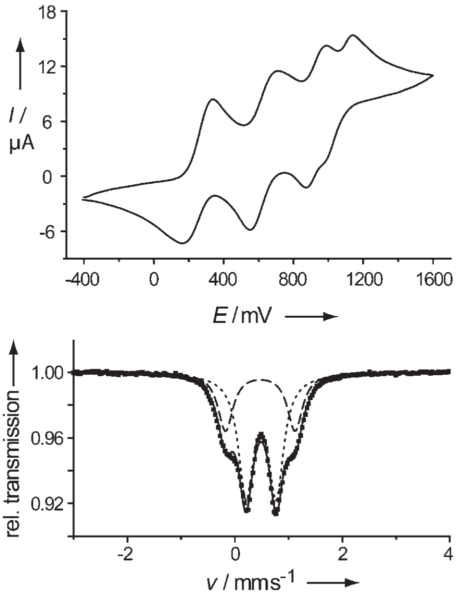


Figure 3. Top: Cyclic voltammogram of **1**, $T=20\,°C$, $\nu=100\,mV\,s^{-1}$. Bottom: Mössbauer spectrum of **1**, $T=-193\,°C$, squares: experiment, solid: simulation, dotted: peripheral Fe^{III}, dashed: central Fe^{III}.

Table 1. Half-wave potentials ($E_{1/2}$ vs. NHE) of **1**–**3**.

	$E_{1/2}$ [mV]			
	I	II	III	IV
1	260	636	930	1063
2	205	541	742	–
3	330	531	–	–

The cyclic voltammogram (CV) of **1** exhibits four quasi-reversible oxidation waves, each involving a one-electron-transfer process corresponding to the Mn^{II}/Mn^{III} redox couples (Figure 3, Table 1). The peak current of all four waves increases linearly with the square root of the scan speed, indicating that the oxidation reactions are diffusion controlled processes. This result suggests that in **1** all the four redox-active Mn^{II} ions are located at the periphery of the ring and one Fe^{III} ion is placed at the center. To ensure that the fourth wave does not result from an oxidation of one of the peripheral Fe^{III} ions, the CV of the all-iron wheel $[Fe^{III}_6Cl_6(L^1)_6]$[21] was recorded under identical conditions as control experiment. However, it did not give any Fe^{III}/Fe^{IV} oxidation waves in the given range. It is worth mentioning that in multisweep experiments under thin-layer conditions, all four redox waves of **1** revealed complete reversibility over several cycles.

The Mössbauer spectrum of **1** at −193 °C and $B=0$ T exhibits two quadrupolar doublets with an area ratio of 1:2 for the three Fe^{III} ions (Figure 3). The doublet with a quadrupole splitting of $\Delta E_Q=0.56(3)\,mm\,s^{-1}$, an isomeric shift of $\delta=0.49(3)\,mm\,s^{-1}$, and a linewidth of $\Gamma=0.34(3)\,mm\,s^{-1}$ is consistent with the two peripheral high-spin Fe^{III} species (relative intensity: 67(3) %), whereas the doublet with the quadrupole splitting of $\Delta E_Q=1.29(3)\,mm\,s^{-1}$, the isomeric shift of $\delta=0.47(3)\,mm\,s^{-1}$, and a linewidth of $\Gamma=0.34(3)\,mm\,s^{-1}$ corresponds to the central high-spin Fe^{III} species (relative intensity: 33(3) %). Thus, the Mössbauer data totally match the proposed placement of the iron ions in structure **1**.

The structure of the $\mathbf{2}^-$ ion (molecule symmetry C_3) is similar to that of centrosymmetric $\mathbf{1}^-$. In $\mathbf{2}^-$ the six-membered ring consists of three Mn^{II} and three In^{III} ions chelated by one nitrogen, one chloride, two μ_2-, and two μ_3-oxygen donors. Unequivocal localization of the Mn^{II} and In^{III} ions in $\mathbf{2}^-$ by X-ray analysis is not possible. Each metal site in the ring is composed of 50 % Mn^{II} and 50 % In^{III} ions (Figure 1S in the Supporting Information). However, the central metal was unambiguously characterized as Mn^{II}. It has a distorted octahedral coordination and is surrounded by six inner μ_3-O donors. The Mn1−O distances (2.212(4)–2.241(4) Å) are in the range commonly found for six-coordinate Mn^{II}-centered wheels.[6,7]

The crystals of **1** and **2** are homogeneous, whereas **3** co-crystallizes with $[In^{III}_6Cl_6(L^1)_6]$.[8] The mixed crystal which contains the two neutral complexes share a single site on an inversion center and thus exhibit crystallographically imposed centrosymmetry. In **3**, an Mn^{II} ion occupies the center of the ring in a distorted octahedral coordination, while two Mn^{II} and four In^{III} ions, chelated by one nitrogen, one chloride, two μ_2-, and two μ_3-oxygen donors, form a six-membered ring. The peripheral Mn^{II} and In^{III} ions in **3** are distributed over all the metal sites. However, with a significant preference of two positions out of the six being occupied by Mn^{II} ions (distribution of Mn^{II} over the three independent ring positions is 26:14:14), suggesting the three Mn^{II} ions are located along the diameter of the wheel. The distances between the central Mn^{II} ion and the inner μ_3-O donor atoms range from 2.330(3) to 2.405(3) Å and are significantly longer than those in $\mathbf{2}^-$ as well as in other Mn^{II}-centered wheels.[6,7] This might be due to superposition of the two molecular wheels **3** and $\{In_6\}$, which in turn resulted in only an average distance for each Mn−O bond. The second component of the crystal structure is composed of $[In^{III}_6Cl_6(L^1)_6]$ and forms basically the same structure as **3**, but featuring exclusively In^{III} ions in the six-membered ring and an empty ring center (Figure 2S in the Supporting Information).

Complex **2** exhibits three quasi-reversible waves (Figure 4, Table 1) that are attributed to the subsequent oxidation of three Mn^{II} ions located at the periphery of the ring. Similar results have already been observed for mixed-valent $\{Mn_7\}^-$ ionic wheels, in which the three Mn^{II} and three Mn^{III} ions are alternately positioned in the ring.[6] Analogously, we also favor an identical configuration for **2**. This arrangement is also supported by Coulomb's law.

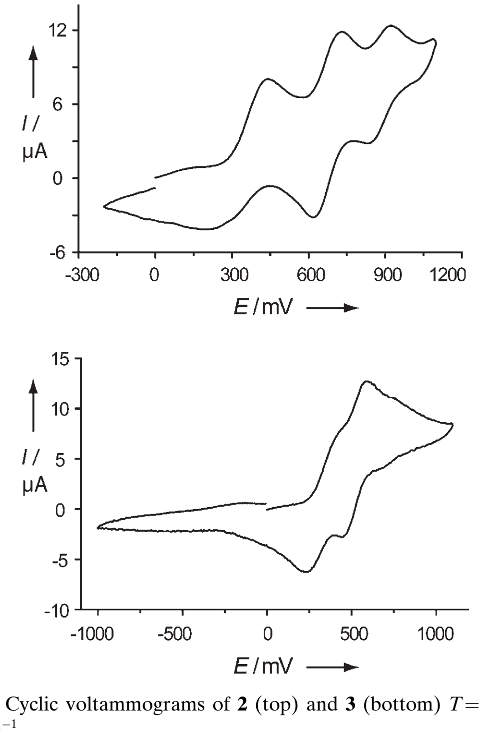


Figure 4. Cyclic voltammograms of **2** (top) and **3** (bottom) $T = 20\,°C$, $\nu = 100\,mV\,s^{-1}$.

The CV of **3** typically exhibits two quasi-reversible one-electron Mn^{II}/Mn^{III} redox waves. This is consistent with two Mn^{II} ions being located at the rim. The $E_{1/2}$ values of **3** are more positive than those of the neutral complex $\{Mn_7\}$.[7] As expected, the central Mn^{II} ions in both **2** and **3** did not undergo oxidation in the given potential range.[6,7,12] In successive-scan experiments, all the redox waves of **2** and **3** showed complete reversibility over several cycles. The large potential displacement (several hundred mV) between the individual oxidation reactions indicates a strong electronic coupling in solution between the crystallographically equivalent manganese ions.

Conclusion

In summary, we have presented new heterometallic, heptanuclear, metal-centered, six-membered, mixed-valent anionic wheels $[PPh_4]\{Fe^{III}\subset[Fe^{III}_2Mn^{II}_4Cl_6(L^1)_6]\}$ (**1**) and $[PPh_4]\{Mn^{II}\subset[Mn^{II}_3In^{III}_3Cl_6(L^1)_6]\}$ (**2**), and neutral wheel $\{Mn^{II}\subset[Mn^{II}_2In^{III}_4Cl_6(L^1)_6]\}$ (**3**). The structures of the complexes **1**–**3** were solved by the combination of FAB-mass spectrometry, single-crystal X-ray analysis, cyclic voltammetry, and Mössbauer spectroscopy. In **1**, four Mn^{II} ions in the periphery are arranged in pairs alternating with one Fe^{III} ion each, whereas in **2**, three Mn^{II} ions alternate with three In^{III} ions and in **3** four In^{III} ions are arranged in pairs alternating with one Mn^{II} ion each. The center of **1** is occupied by an Fe^{III} ion, whereas in the center of **2** and **3**, an Mn^{II} ion is located. The new method can be used conveniently to generate a variety of heterometallic wheels with predetermined metal ratios, previously not possible.

Experimental Section

Materials and methods: All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. HPLC grade solvents were obtained from ACROS and used without further purification. Infrared spectra were obtained from a Perkin–Elmer 1620 FT-IR spectrometer equipped with a 16PC FT-IR. FAB-MS spectra were recorded with a Micromass ZAB-Spec spectrometer. Elemental analyses were performed with an EA 1110 CHNS-Microautomat. Cyclic voltammetric measurements were carried out using an EG&G Princeton Applied Research (PAR) model 264 A potentiostat coupled with a conventional three-electrode cell-assembly consisting of a glassy-carbon working electrode, a platinum-wire reference electrode, and a platinum-rod counter electrode. Measurements were made with approximate $10^{-3}\,M$ solutions of the complexes in CH_2Cl_2 with $0.1\,M$ tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Ferrocene was used as an internal standard $\{E_{1/2}(F_c/F_c) = 410\,mV$ vs. NHE$\}$.[13] The reversibility of the voltammograms and the number of electrons involved in the redox processes were determined as described in the literature.[14] The Mössbauer spectrum was recorded by a Mössbauer Cryostat, Oxford Instruments, equipped with a DTC2 temperature controller. A ^{57}Co in a Rh-matrix was used as the Mössbauer source and an alpha-iron foil was used for calibration. *N*-Benzyldiethanolamine (H_2L^1) and $[PPh_4]_2[MnCl_4]$ were prepared according to literature methods.[15]

$[PPh_4]\{Fe^{III}\subset[Fe^{III}{}_2Mn^{II}{}_4Cl_6(L^1)_6]\}$ (1): Cs_2CO_3 (1.37 g, 4.20 mmol) and H_2L^1 (0.68 g, 3.50 mmol) were stirred in CH_3CN (75 mL) for 2 h at 20 °C. A solution of $[PPh_4]_2[MnCl_4]$ (2.03 g, 2.31 mmol) and $FeCl_3$ (0.28 g, 1.73 mmol) in CH_3CN (20 mL) was added to this suspension. Immediately, the color of the mixture changed to pale yellow, and the mixture was stirred for a further 7 d. During this time, the color changed to brown-yellow. The reaction mixture was filtered through a cannula. The CH_3CN filtrate was evaporated under reduced pressure, the resulting dry residue was treated with THF (50 mL), and insoluble PPh_4Cl was removed by filtration. The remaining solution was concentrated to about 2 mL and treated with Et_2O (25 mL). Brown-yellow microcrystals were collected, washed with Et_2O (20 mL), and dried in vacuo. Yield: 0.56 g (47 %). X-ray quality crystals were grown (8 d) from a CH_2Cl_2/Et_2O (1:8 v/v) solvent mixture at −20 °C. IR (KBr): $\tilde{\nu}=3421$, 3049, 3014, 2855, 1495, 1437, 1350, 1261, 1077, 981, 907, 803, 761, 724, 704, 668, 614, 526 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z* (%): 2061 (8) $[M]^+$, 1758 (45) $[Mn_4Fe_3Cl_6(L^1)_6]^+$, 1723 (65) $[Mn_4Fe_3Cl_5(L^1)_6]^+$, 1688 (50) $[Mn_4Fe_3Cl_4(L^1)_6]^+$, 1530 (100) $[Mn_4Fe_3Cl_5(L^1)_5]^+$, 1494 (45) $[Mn_4Fe_3Cl_4(L^1)_5]^+$, 1404 (45) $[Mn_3Fe_3Cl_3(L^1)_5]^+$, 1337 (45) $[Mn_4Fe_3Cl_4(L^1)_4]^+$, 1246 (70) $[Mn_4Fe_2Cl_3(L^1)_4]^+$, 1118 (60) $[Mn_4FeCl_2(L^1)_4]^+$, 835 (95) $[Mn_3FeCl(L^1)_3]^+$; elemental analysis calcd (%) for $C_{90}H_{110}Cl_6Fe_3Mn_4N_6O_{12}P{\cdot}H_2O$: C 51.01, H 5.34, N 3.98; found C 50.92, H 5.37, N 3.97.

$[PPh_4]\{Mn^{II}\subset[Mn^{II}{}_3In^{III}{}_3Cl_6(L^1)_6]\}$ (2): Cs_2CO_3 (0.65 g, 2.02 mmol) and H_2L^1 (0.33 g, 1.70 mmol) were stirred in CH_3CN (50 mL) at 20 °C for 2 h. A solution of $[PPh_4]_2[MnCl_4]$ (0.99 g, 1.13 mmol) and $InCl_3$ (0.19 g, 0.85 mmol) in CH_3CN (20 mL) was added to this suspension. Immediately, the color of the mixture changed to pale pink, and stirring was continued for 5 d. During this time, the color changed to red-brown. Further workup of this mixture, as in **1**, afforded red-brown microcrystalline **2**. Yield: 0.16 g (24 %). Single crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into a solution of **2** in CH_2Cl_2 after 10 d. IR (KBr): $\tilde{\nu}=3439$, 3055, 3018, 2856, 1620, 1494, 1435, 1347, 1299, 1104, 1074, 1045, 982, 901, 757, 702, 613, 525 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z* (%): 2274 (7) $[M]^+$, 2238 (16) $[M{-}Cl]^+$, 1936 (25) $[Mn_4In_3Cl_6(L^1)_6]^+$, 1900 (65) $[Mn_4In_3Cl_5(L^1)_6]^+$, 1865 (55) $[Mn_4In_3Cl_4(L^1)_6]^+$, 1741 (40) $[Mn_4In_3Cl_6(L^1)_5]^+$, 1519 (35) $[Mn_4In_2Cl_3(L^1)_5]^+$, 1177 (65) $[Mn_4InCl_2(L^1)_4]^+$, 834 (100) $[Mn_4Cl(L^1)_3]^+$; elemental analysis calcd (%) for $C_{90}H_{110}Cl_6In_3Mn_4N_6O_{12}P$: C 47.50, H 4.87, N 3.69; found C 47.75, H 4.40, N 3.62.

$\{Mn^{II}\subset[Mn^{II}{}_2In^{III}{}_4Cl_6(L^1)_6\}$ (3): H_2L^1 (0.33 g, 1.70 mmol) was added to a suspension of Cs_2CO_3 (0.65 g, 2.02 mmol) in CH_3CN (50 mL) at 20 °C. After stirring the suspension for 2 h, a solution of $[PPh_4]_2[MnCl_4]$ (0.75 g, 0.85 mmol) and $InCl_3$ (0.25 g, 1.13 mmol) in CH_3CN (20 mL) was added. The color of the mixture changed to pale pink, and was stirred for a further 7 d. During this time, the color of the suspension changed to violet-gray. The suspension was filtered and the residue was extracted with CH_2Cl_2 (50 mL). The extract was concentrated (2 mL), and treated with Et_2O (30 mL). The precipitate was collected, washed with Et_2O (20 mL), dried in vacuo, and recrystallized by diffusion of pentane into the solution of **3** in $CHCl_3$ to give violet-gray microcrystals of **3**$\cdot CHCl_3$ within 4 d. Yield: 0.24 g (39 %). IR (KBr): $\tilde{\nu}=3439$, 2968, 1915, 2856, 1620, 1380, 1258, 1089, 1045, 975 cm^{-1}; MS (FAB, *m*-NBA): *m*/*z* (%): 1996 (65) $[M]^+$, 1960 (80) $[M{-}Cl]^+$, 1337 (100) $[In_4Cl_3(L^1)_4)]^+$; elemental analysis calcd (%) for $C_{66}H_{90}Cl_6In_4Mn_3N_6O_{12}{\cdot}CHCl_3$: C 37.54, H 4.27, N 3.92; found C 37.61, H 4.01, N 3.94.

Pink-gray crystals composed of {54 % **3**·46 % $[In^{III}{}_6Cl_6(L^1)_6]\}$ ·3.5 CH_2Cl_2, suitable for X-ray structure analysis were obtained after two weeks by slow vapor diffusion of pentane into a solution of **3**$\cdot CHCl_3$ in CH_2Cl_2.

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft Sa 276/27–2, SFB 583, GK 312, SPP 1137, the Bayerisches Langzeitprogramm Neue Werkstoffe, and the Fonds der Chemischen Industrie are gratefully acknowledged. The authors acknowledge the contributions of Dr. Takayuki Nakajima in the preliminary stages of this project. We thank Dr. M. Moll, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, for generous allocation of cyclic voltammetric facilities.

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[8] Suitable single crystals were embedded in protective perfluoro polyether oil and transferred to the cold gas stream of the diffractometer. Data were collected on a Bruker-Nonius KappaCCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), and a graphite monochromator. A semi-empirical absorption correction based on multiple scans (SADABS)[16] was performed for **1**·6.08 CH_2Cl_2 and the mixed crystal {54 % **3**·46 % $[In^{III}{}_6Cl_6(L^1)_6]$}·3.5 CH_2Cl_2, while a Scalepack absorption correction was applied for **2**·Et_2O·CH_2Cl_2·6 H_2O. The structures were solved by direct methods, full-matrix least-squares refinements were carried out on F^2 using either SHELXTL NT 6.12[17] or SHELXL-97.[18] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms in **1**, **2**, and **3**·$[In^{III}{}_6Cl_6(L^1)_6]$ were geometrically positioned using a riding model with their isotropic displacement parameters being 1.5 U(eq) of the proceeding C or N atom. Both the PPh_4^+ ion and the CH_2Cl_2 molecules in **1** are disordered. Two alternative sites for the PPh_4^+ ion were refined to give occupancies of 78.3(5) and 21.7(5) %, respectively. The crystal structure contained approximately 6.08 molecules of CH_2Cl_2 spread over 11 different crystallographic sites. The remaining significant residual electron density maxima were to be found in close proximity of the disordered structure parts and indicate the presence of further disorder, which could not be resolved in a reasonable way. A number of restraints (SAME, DFIX, SIMU, ISOR) were applied in the treatment of the disorder. The Et_2O molecule in **2** was disordered, and two alternative sites were refined to 50:50 %. An Mn/In atom disorder model with 50 % occupation on each metal position of the six-membered ring was proposed. One Mn^{II} atom was found in the center of the ring. In the mixed crystal of (54 % **3**·46 % $[In^{III}{}_6Cl_6(L^1)_6]$)·3.5 CH_2Cl_2, the ratio of 54:46 was initially derived on the basis of the refined occupancy of 54 % for the central Mn^{II} ion and proved to be consistent with a total of 4.92 In^{III} and 1.08 Mn^{II} ions in the ring resulting from a subsequent refinement of the ring atom occupancy factors. A number of crystals examined showed the same behavior with slightly different ratios of the two components. Two of the phenyl rings of the ligand were disordered with two alternative orientations of 57(2) and 43(2) % occupancy. The CH_2Cl_2 solvate molecules were also disordered. While one of the symmetrically independent CH_2Cl_2 molecules occupied two alternative sites (64(2):36(2) %), the remaining solvate molecules were distributed over three sites with a resulting total occupancy of 75 % (34.5(4):19.3(4):21.2(4) %). SAME and ISOR restraints were applied in their refinement. CCDC-285291 (**1**), CCDC-279215 (**2**), and CCDC-279216 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[9] Crystallographic data for **1**·6.08 CH_2Cl_2 ($C_{96.08}H_{122.16}Cl_{18.16}Fe_3Mn_4N_6O_{12}P$): $M_r = 2614.99$ g mol^{-1}, $T = 100(2)$ K, crystal size $0.35 \times 0.17 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 15.934(3)$, $b = 16.300(1)$, $c = 26.370(3)$ Å, $\alpha = 86.38(1)$, $\beta = 88.28(2)$, $\gamma = 61.50(1)°$, $V = 6006.9(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.446$ g cm^{-3}, $\mu = 1.231$ mm^{-1}, $F(000) = 2677$, $6.34 < 2\theta < 51.36°$, min/max transmission = 0.712/1.000, 78848 collected reflections, 22151 unique reflections [R(int) = 0.0511], 13516 observed reflections [$I > 2\sigma(I)$], 1540 parameters, $R1 = 0.0921$ [$I > 2\sigma(I)$], w$R2 = 0.2872$ (all data), largest diff. peak/hole 1.709/-0.926 e Å^{-3}.

[10] Crystallographic data for **2**·Et_2O·CH_2Cl_2·6 H_2O ($C_{93}H_{129}Cl_8In_3Mn_4N_6O_{18.5}P$): $M_r = 2505.81$ g mol^{-1}, $T = 173(2)$ K, crystal size $0.35 \times 0.25 \times 0.15$ mm^3, triclinic, space group $P\bar{1}$, $a = 16.5135(4)$, $b = 18.0023(3)$, $c = 22.2813(6)$ Å, $\alpha = 101.475(1)$, $\beta = 101.127(1)$, $\gamma = 114.518(1)°$, $V = 5617.0(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.482$ g cm^{-3}, $\mu = 1.306$ mm^{-1}, $F(000) = 2550$, $5.02 < 2\theta < 50.04°$, min/max transmission = 0.6579/0.8282, 37346 measured reflections, 19628 unique reflections, 12996 observed reflections [$I > 2\sigma(I)$], 1216 parameters, $R1 = 0.0619$ [$I > 2\sigma(I)$], w$R2 = 0.1979$ (all data), largest diff. peak/hole 1.334/-0.869 e Å^{-3}.

[11] Crystallographic data for 54 % **3**·46 % $[In^{III}{}_6Cl_6(L^1)_6]$·3.5 CH_2Cl_2 ($C_{69.50}H_{93.50}Cl_{16.50}In_{4.92}Mn_{1.62}N_6O_{12}$): $M_r = 2443.61$ g mol^{-1}, $T = 100(2)$ K, crystal size $0.18 \times 0.18 \times 0.08$ mm^3, monoclinic, space group $P2_1/c$, $a = 16.936(2)$, $b = 16.966(2)$, $c = 16.234(2)$ Å, $\alpha = 90$, $\beta = 107.604(8)$, $\gamma = 90°$, $V = 4446.2(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.825$ g cm^{-3}, $\mu = 2.031$ mm^{-1}, $F(000) = 2421$, $6.54 < 2\theta < 54.20°$, min/max transmission = 0.814/1.000, 104036 collected reflections, 9796 unique reflections [R(int) = 0.0837], 7116 observed reflections [$I > 2\sigma(I)$], 678 parameters, $R1 = 0.0352$ [$I > 2\sigma(I)$], w$R2 = 0.0776$ (all data), largest diff. peak/hole 0.874/-0.817 e Å^{-3}.

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Received: December 1, 2005