Diamagnetic and Paramagnetic Keggin Polyoxometalate Salts Containing 1-D and 3-D Decamethylferrocenium Networks: Preparation, Crystal Structures, and Magnetic Properties of $[Fe(C_5Me_5)_2]_4(POM)(solv)_n$ (POM = $[SiMo_{12}O_{40}]^{4-}$, $[SiW_{12}O_{40}]^{4-}$, $[PMo_{12}O_{40}]^{4-}$, $[HFeW_{12}O_{40}]^{4-}$; solv = H_2O, C_3H_7ON, CH_3CN)

P. Le Maguerès,[1a] L. Ouahab,*,[1a] S. Golhen,[1a] D. Grandjean,[1a] O. Peña,[1a] J.-C. Jegaden,[1a] C. J. Gomez-Garcia,[1b,c] and P. Delhaès*,[1b]

Laboratoire de Chimie du solide et Inorganique Moléculaire, URA 1495 CNRS, Université de Rennes I, 35042 Rennes Cédex, France, and Centre de Recherche Paul Pascal (CNRS), avenue Albert Schweitzer, 33600 Pessac, France

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The synthesis, X-ray crystal structures, EPR, and magnetic properties of the salts formulated $[Fe^{III}(C_5Me_5)_2]_4(POM)(solv)_n$, with POM = $[SiMo^{VI}_{12}O_{40}]^{4-}$ (**1**), $[SiW^{VI}_{12}O_{40}]^{4-}$ (**2**), $[PMo^{V}Mo^{VI}_{11}O_{40}]^{4-}$ (**3**), and $[HFeW_{12}O_{40}]^{4-}$ (**4**) and solv = H_2O, C_3H_7ON (DMF), or CH_3CN, are reported. Salts **1**−**3** are isostructural and crystallize in the triclinic space group $P\bar{1}$. Crystal data for **1**: $a = 14.247(11)$ Å, $b = 15.004(4)$ Å, $c = 15.418(2)$ Å, $\alpha = 63.26(2)°$, $\beta = 83.41(3)°$, $\gamma = 69.77(4)°$, $V = 2758(2)$ Å^3, $Z = 1$, $R = 0.062$ for 4662 observed reflections with $I \geq 6\sigma(I)$. Salt **4** crystallizes in the monoclinic space group $C2/c$, with $a = 29.495(9)$ Å, $b = 12.545(4)$ Å, $c = 29.482(4)$ Å, $\beta = 94.39(4)°$, $V = 10877(10)$ Å^3, $Z = 4$, and $R = 0.045$ for 5305 observed reflections with $I \geq 6\sigma(I)$. In salts **1**−**3**, the $[Fe(C_5Me_5)_2]^+$ cations form linear chains which surround columns of the POM. Salt **4** presents a 3-D structure where the $[Fe(C_5Me_5)_2]^+$ occupy the vertices of a cuboctahedron. The 3-D structure results from the association of these cuboctahedrons by sharing vertices in the *a* and *c* directions and faces in the *b* direction. The magnetic properties of these compounds between 2−300 K indicate that the four salts present very weak magnetic interactions obeying the Curie−Weiss expression $\chi = C/(T - \Theta)$ with small values for Θ (**1**, $C = 3.118$ emu·mol^{-1}, $\Theta = -1.9$ K, $\mu_{eff} = 2.497\ \mu_B$; **2**, $C = 3.113$ emu·mol^{-1}, $\Theta = -4.5$ K, $\mu_{eff} = 2.495\ \mu_B$; **3**, $C = 3.727$ emu·mol^{-1}, $\Theta = -3.2$ K, $\mu_{eff} = 2.556\ \mu_B$ for the organic radicals and $\mu_{eff} = 1.916\ \mu_B$ for the inorganic anions; **4**, $C = 6.887$ emu·mol^{-1}, $\Theta = -0.2$ K, $\mu_{eff} = 2.295\ \mu_B$ for the organic radicals and $\mu_{eff} = 5.834\ \mu_B$ for the inorganic anions). The low *T* magnetization data as well as the EPR spectra also support the absence of magnetic exchange interactions between the two parts. Thus, for compound **4** the magnetization curve at 2 K can be very well reproduced from the sum of contributions of the Fe^{III}-containing Keggin anion (with $S = {}^5/_2$ and $g = 1.992$) and the four $[Fe(C_5Me_5)_2]^+$ radicals (with $S = {}^1/_2$ and $g = 2.539$). In the EPR spectra the typical signals of both ionic fragments are observed.

Introduction

Polyoxometalates (POM) are molecular blocks of metal oxide formed by MoO_6 and WO_6 octahedra sharing vertices or edges.[2] Due to the richness of their structural and electronic properties, great interest is currently focused in these inorganic anions in many fields of research such as catalysis, biology, medicine and materials science.[3,4] In previous works, we have succeeded in the use of polyoxometalates as components in charge transfer salts.[5] We have, in particular, characterized compounds containing mobile and localized magnetic electrons.[6] Our contribution concerns currently new salts obtained by the association of polyoxometalates with the organometallic decamethylferrocenium radical cation. We are dealing in this report with POM formulated as $[X^{+n}M_{12}O_{40}]^{(8-n)-}$ (M = Mo^{VI}, W^{VI}; X = Si, P, Fe, ...) presenting the Keggin[7] structure. This latter results from the association of four M_3O_{13} units tetrahedrally surrounding the central atom X.

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(1) (a) Université de Rennes I. (b) Centre de Recherche Paul Pascal (CNRS). (c) Permanent address: Departamento de Quimica Inorgánica. Univ. de Valencia, Dr Moliner, E-46100 Burjasot, Spain.

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The decamethylferrocene is a good organometallic donor that leads to the decamethylferrocenium cation ($S = {}^1/_2$).[8-10] Miller et al.[10] discovered a new class of molecular ferromagnets by its association with the organic acceptor TCNE (tetracyanoethylene). These molecular-based magnetic materials contain either 1-D mixed stacks of donors and acceptors, or linear or two-dimensional ferrimagnetic bimetallic networks.[11,12] It is well established that the increase in the magnetic dimensionality is necessary to raise the critical temperature (T_c) below which the compounds exhibit spontaneous magnetization.[13-15]

We report in this paper the synthesis, crystal structures and magnetic properties of the compounds formulated $[Fe^{III}(C_5Me_5)_2]_4(POM)(solv)_n$, (POM = $[SiMo^{VI}_{12}O_{40}]^{4-}$ (**1**), $[SiW^{VI}_{12}O_{40}]^{4-}$ (**2**), $[PMo^{V}Mo^{VI}_{11}O_{40}]^{4-}$ (**3**), $[HFeW_{12}O_{40}]^{4-}$ (**4**); solv = H_2O, C_3H_7ON (DMF), CH_3CN). These four salts account for the potentialities of Keggin POM. The Keggin anions in compounds **1** and **2** are diamagnetic and contain Mo^{VI} or W^{VI} metals. In compound **3** the POM is paramagnetic as a result of a one electron reduction, while in compound **4** the polyanion contains a paramagnetic tetrahedral Fe^{III} atom ($S = {}^5/_2$) in its central cavity. Additionally, we give the detailed structure of a Keggin anion containing a Fe^{III} atom in its central cavity.

Experimental Section

Preparation of compounds. $(Bu_4N)_4[SiM_{12}O_{40}]$ (M = Mo, W), $(Bu_4N)_3[PMo_{12}O_{40}]$, $(Bu_4N)_4H[FeW_{12}O_{40}]$ and $[Fe(C_5Me_5)_2]BF_4$ were prepared as described in the literature.[16,22b]

$[Fe(C_5Me_5)_2]_4[SiMo_{12}O_{40}](DMF)$ (1), $[Fe(C_5Me_5)_2]_4[SiW_{12}O_{40}](DMF)_2$ (2) and $[Fe(C_5Me_5)_2]_4[HFeW_{12}O_{40}](CH_3CN)\cdot 3H_2O$ (4). The mixture of acetonitrile solutions of $(Bu_4N)_4[XM_{12}O_{40}]$ (0.25 mmol in 30 mL) and $[Fe(C_5Me_5)_2]BF_4$ (1.0 mmol in 10 mL) gives blue green precipitates which are filtered and recrystallized in DMF for compounds **1** and **2** and in CH_3CN for **4**.

Table 1. Crystallographic Data for $[Fe(C_5Me_5)_2]_4SiMo_{12}O_{40}(NMe_2CHO)$ (**1**) and $[Fe(C_5Me_5)_2]_4HFeW_{12}O_{40}(MeCN)\cdot 3H_2O$ (**2**)

	1	**2**
formula	$Fe_4Mo_{12}SiO_{41}NC_{83}H_{127}$	$Fe_5W_{12}O_{43}C_{82}H_{127}$
a, Å	14.247(11)	29.495(9)
b, Å	15.004(4)	12.545(4)
c, Å	15.418(2)	29.482(24)
α, deg	63.26(2)	
β, deg	83.41(3)	94.39(4)
γ, deg	69.77(4)	
V, Å^3	2758(2)	10877(10)
Z	1	4
fw	3197.7	4286.3
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
T, °C	293	293
d_{calc}, g·cm^{-3}	1.925	2.617
μ(Mo Kα), cm^{-1}	18.773	136.30
R^a	0.062	0.045
$R_w{}^b$	0.089	0.059

[a] $R = \sum[||F_o| - F_c||]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w = 4F_o^2/[\sigma^2(I) + (0.07|F_o|^2)^2]$.

$[Fe(C_5Me_5)_2]_4[PMo_{12}O_{40}](DMF)_2$ (3). To an acetonitrile solution (0.2 mmol in 30 mL) of $(Bu_4N)_3[PMo_{12}O_{40}]$ was added dropwise an ether solution (0.6 mmol in 20 mL) of $[Fe(C_5Me_5)_2]$. The blue green precipitate was filtered and recrystallized in DMF. The stoichiometries were assumed on the basis of the crystal structure analysis. It will be noted that the 4:1 (cation:anion) stoichiometries are obtained independently of the charges of the anions. The redox reaction occurs in the case of highly acceptor polyanions like $[PMo_{12}O_{40}]^{3-}$, giving rise to the paramagnetic species $[PMo^{V}Mo^{VI}_{11}O_{40}]^{4-}$.

Crystallographic Data Collection and Structure Determination. Green crystals of compounds **1** and **4** were mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The cell dimensions have been refined by least-squares method from setting angles of 25 centered reflections ($8 \leq 2\theta \leq 15°$). The crystal data are summarized in Table 1. The intensities were collected by $\theta-2\theta$ scans. Three standard reflections were measured every hour and revealed no fluctuations in intensities. The Lorentz and polarization corrections were applied. The absorption correction was performed using the DIFABS procedure.[17a]

The structures were solved by direct method and successive Fourier difference synthesis and refined by the full matrix least-squares method. After refinement of positional and anisotropic (β_{ij}) thermal parameters for non-hydrogen atoms, the positions of the H-atoms were calculated (d(C–H) = 1 Å; $B_{eq} = 5$ Å^2) and included as a fixed contribution to F_c. Scattering factors and corrections for anomalous dispersion were taken from ref 17b. All the calculations were performed on a MicroVax 3100 computer using the Enraf-Nonius MoLen programs.[17c] Atomic coordinates and selected bond lengths for both structures are given in Tables 2 and 3. The complete crystal structure results are given as supplementary material.

Magnetic and EPR Spectroscopy Measurements. Magnetic measurements were made on polycrystalline samples with

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Table 2. Fractional Atomic Coordinates and Their Equivalent Isotropic Thermal Parameters[a]

	x	*y*	*z*	B_{eq}, Å^2		*x*	*y*	*z*	B_{eq}, Å^2
(a) $[Fe(C_5(CH_3)_5)_2]_4SiMo_{12}O_{40}[(CH_3)_2NCHO]$									
Si	0.000	0.000	0.000	2.5(1)	O9	0.1960(9)	−0.3411(7)	0.2933(7)	6.0(3)
Mo1	−0.0941(1)	0.23844(7)	0.01871(7)	4.16(3)	O10	−0.059(1)	−0.0336(8)	0.247(1)	10.1(4)
Mo2	0.1297(1)	−0.23275(8)	0.20084(8)	4.19(3)	O11	0.149(1)	0.063(1)	0.1284(9)	9.1(5)
Mo3	0.0583(1)	0.01050(9)	0.20979(8)	5.42(4)	O12	0.077(1)	0.0168(7)	0.3097(6)	7.5(3)
Mo4	−0.1261(1)	−0.0979(1)	0.2142(1)	6.37(5)	O13	−0.225(1)	0.0212(8)	0.1411(7)	9.1(4)
Mo5	−0.2611(1)	0.1179(1)	0.00433(9)	4.71(4)	O14	−0.155(1)	−0.1629(8)	0.1380(8)	9.3(5)
Mo6	0.1629(1)	0.1361(1)	−0.0131(1)	6.10(4)	O15	−0.182(1)	−0.155(1)	0.3147(8)	9.7(5)
O1	−0.1145(9)	0.2863(8)	−0.1194(6)	7.5(3)	O16	−0.3819(8)	0.171(1)	0.0104(8)	7.8(4)
O2	−0.0448(9)	0.150(1)	0.1423(8)	8.6(5)	O17	−0.260(1)	0.0053(8)	−0.0122(8)	9.5(5)
O3	−0.2084(9)	0.2042(8)	0.0361(6)	7.5(3)	O18	0.2413(9)	0.1922(8)	−0.010(1)	8.9(4)
O4	0.042(1)	0.232(1)	−0.0179(9)	9.0(5)	O19	0.016(1)	−0.0627(9)	0.1194(9)	2.4(4)
O5	−0.137(1)	0.3559(6)	0.0209(7)	6.5(3)	O20	−0.105(1)	−0.019(1)	0.042(1)	2.9(4)
O6	0.132(1)	−0.1278(7)	0.2400(9)	9.4(4)	O21	−0.091(1)	0.1089(9)	−0.029(1)	2.6(4)
O7	0.0011(9)	−0.2179(8)	0.242(1)	8.6(4)	O22	0.020(1)	0.0751(9)	0.039(1)	2.8(4)
O8	−0.2420(9)	0.1977(8)	−0.1220(6)	7.5(3)					
$Fe(C_5(CH_3)_5)_2$ [a]									
Fe1	0.3501(1)	0.2966(1)	0.2788(1)	3.16(5)	C11	0.194(1)	0.367(1)	0.273(1)	4.7(4)
C1	0.492(1)	0.254(1)	0.3411(9)	4.2(4)	C12	0.219(1)	0.316(1)	0.216(1)	5.5(5)
C2	0.439(1)	0.3642(9)	0.3098(9)	3.6(3)	C13	0.270(1)	0.206(1)	0.278(1)	7.4(5)
C3	0.4206(9)	0.4130(9)	0.2089(9)	3.5(3)	C14	0.268(1)	0.203(1)	0.372(1)	7.4(6)
C4	0.457(1)	0.336(1)	0.1772(9)	4.2(4)	C15	0.222(1)	0.302(1)	0.3639(9)	5.2(4)
C5	0.501(1)	0.2365(9)	0.2567(9)	4.2(4)	C16	0.136(2)	0.484(2)	0.236(2)	9.7(6)*
C6	0.527(1)	0.173(1)	0.442(1)	6.1(4)*	C17	0.200(2)	0.359(2)	0.107(2)	10.2(7)*
C7	0.414(1)	0.417(1)	0.377(1)	5.2(4)*	C18	0.308(2)	0.115(2)	0.255(2)	11.2(8)*
C8	0.373(1)	0.529(1)	0.147(1)	5.4(4)*	C19	0.306(2)	0.111(2)	0.468(2)	12.6(9)*
C9	0.457(1)	0.353(1)	0.073(1)	7.2(5)*	C20	0.202(2)	0.333(2)	0.445(2)	10.5(7)*
C10	0.556(1)	0.129(1)	0.257(1)	6.3(4)*					
$Fe(C_5(CH_3)_5)_2$ [b]									
Fe2	0.8134(1)	0.3766(1)	0.3482(1)	3.27(5)	C31	0.914(1)	0.444(1)	0.254(1)	6.1(5)
C21	0.677(1)	0.3894(9)	0.4191(8)	3.9(3)	C32	0.957(1)	0.345(1)	0.292(1)	6.1(4)
C22	0.726(1)	0.285(1)	0.440(1)	4.9(4)	C33	0.963(1)	0.303(1)	0.389(1)	5.8(5)
C23	0.738(1)	0.280(1)	0.345(1)	5.6(5)	C34	0.929(1)	0.385(1)	0.417(1)	6.2(4)*
C24	0.696(1)	0.382(1)	0.274(1)	5.1(4)	C35	0.889(1)	0.478(1)	0.327(1)	8.3(5)
C25	0.659(1)	0.447(1)	0.318(1)	5.4(5)	C36	0.889(2)	0.520(2)	0.142(2)	12.0(8)*
C26	0.647(2)	0.435(1)	0.486(1)	8.4(6)*	C37	0.990(2)	0.281(2)	0.240(2)	12.6(9)*
C27	0.757(2)	0.192(2)	0.537(2)	9.4(6)*	C38	1.011(2)	0.198(2)	0.462(2)	13(1)*
C28	0.786(2)	0.180(1)	0.332(1)	8.3(6)*	C39	0.904(3)	0.417(3)	0.500(2)	16(1)*
C29	0.688(2)	0.406(1)	0.168(1)	8.5(6)*	C40	0.840(3)	0.593(3)	0.307(3)	18(1)*
C30	0.606(2)	0.562(2)	0.263(2)	8.7(6)*					
DMF									
O1S	0.560(2)	0.755(2)	0.374(2)	7.3(7)*	C2S	0.430(2)	0.845(2)	0.235(2)	5.3(7)*
N1S	0.511(1)	0.862(1)	0.224(1)	1.5(3)*	C3S	0.574(2)	0.817(2)	0.295(2)	4.7(6)*
C1S	0.531(3)	0.924(2)	0.131(2)	6.0(8)*					
(b) $[Fe(C_5(CH_3)_5)_2]_4HFeW_{12}O_{40}{\cdot}3H_2O$									
Fe1	0.000	0.2342(2)	0.250	1.42(7)	O8	−0.1070(4)	0.1446(9)	0.2473(4)	1.8(3)
W1	0.02080(3)	0.03909(5)	0.16899(3)	1.59(1)	O9	−0.1213(4)	−0.0611(9)	0.2113(5)	2.5(3)
W2	−0.07946(3)	0.03581(5)	0.21434(3)	1.58(1)	O10	−0.0061(4)	0.3208(8)	0.1453(5)	1.8(2)*
W3	0.03016(3)	0.42978(5)	0.17293(3)	1.75(1)	O11	0.1274(4)	0.3562(9)	0.2454(5)	2.5(3)
W4	−0.05668(3)	0.22235(5)	0.14060(3)	1.66(1)	O12	0.0838(4)	0.352(1)	0.1590(5)	2.3(3)
W5	−0.08200(3)	0.43311(5)	0.22354(3)	1.80(1)	O13	0.0238(5)	0.4660(8)	0.2986(5)	2.3(3)
W6	0.10720(3)	0.24636(5)	0.20330(3)	1.73(1)	O14	0.0296(5)	0.521(1)	0.1307(5)	3.3(3)
O1	−0.0333(5)	−0.0409(8)	0.1832(5)	2.1(3)	O15	−0.0853(4)	0.3237(9)	0.1778(5)	2.0(3)
O2	−0.0153(4)	0.1113(9)	0.1215(5)	2.5(3)	O16	−0.0832(5)	0.2524(9)	0.0891(5)	2.7(3)
O3	0.0459(4)	−0.0014(8)	0.2298(5)	2.1(3)	O17	−0.1172(5)	0.529(1)	0.1998(6)	3.7(4)
O4	0.0662(4)	0.1487(9)	0.1708(5)	1.7(3)	O18	0.1578(5)	0.218(1)	0.1817(5)	2.9(3)
O5	0.0448(5)	−0.0566(9)	0.1378(5)	2.4(3)	O19	0.0450(4)	0.3179(9)	0.2306(4)	1.5(2)
O6	0.0653(4)	0.5050(9)	0.2212(5)	2.0(3)	O20	−0.0241(4)	0.1500(8)	0.2035(5)	1.5(2)
O7	−0.0975(4)	0.1115(8)	0.1579(5)	1.9(3)					
$Fe(C_5(CH_3)_5)_2$ [a]									
Fe2	0.4130(1)	0.2356(2)	0.0241(1)	1.91(5)	C11	0.3940(9)	0.396(1)	0.0249(9)	3.6(5)
C1	0.4378(8)	0.080(2)	0.0152(9)	3.6(5)	C12	0.3914(9)	0.358(2)	−0.0203(9)	3.9(6)
C2	0.4331(8)	0.100(1)	0.0616(8)	3.2(5)	C13	0.3584(9)	0.270(2)	−0.0226(9)	4.9(6)
C3	0.4617(8)	0.185(2)	0.0748(8)	3.4(5)	C14	0.3426(8)	0.258(2)	0.0232(9)	4.3(6)
C4	0.4837(7)	0.220(2)	0.0361(8)	2.9(5)	C15	0.3636(8)	0.333(1)	0.0502(8)	3.1(5)
C5	0.4692(8)	0.160(2)	−0.0005(9)	3.3(5)	C16	0.423(1)	0.490(2)	0.043(1)	6.5(8)
C6	0.415(1)	−0.007(2)	−0.011(1)	9(1)	C17	0.416(1)	0.403(2)	−0.059(1)	7.3(9)
C7	0.407(1)	0.031(2)	0.090(1)	10(1)	C18	0.346(1)	0.216(2)	−0.066(1)	9(1)
C8	0.467(1)	0.228(2)	0.1240(9)	5.4(7)	C19	0.308(1)	0.180(2)	0.038(1)	10(1)
C9	0.519(1)	0.310(2)	0.036(1)	6.8(8)	C20	0.353(1)	0.346(2)	0.097(1)	9.8(8)
C10	0.486(1)	0.168(2)	−0.0454(9)	5.3(7)					

Table 2 (Continued)

	x	y	z	B_{eq}, Å^2		x	y	z	B_{eq}, Å^2
				$Fe(C_5(CH_3)_5)_2$ [b]					
Fe3	0.2810(1)	0.2540(2)	0.3722(1)	2.89(7)	C33	0.266(1)	0.185(2)	0.309(1)	6.3(8)
C21	0.2308(9)	0.214(2)	0.416(1)	5.7(8)	C34	0.277(1)	0.294(2)	0.301(1)	6.0(7)
C22	0.229(1)	0.322(2)	0.401(1)	7(1)	C35	0.3190(9)	0.312(2)	0.321(1)	5.9(8)
C23	0.271(1)	0.370(2)	0.420(1)	6.4(8)	C36	0.388(1)	0.197(2)	0.358(1)	6.2(8)
C24	0.296(1)	0.292(2)	0.440(1)	6.3(8)	C37	0.314(1)	0.023(3)	0.339(1)	10(1)
C25	0.274(1)	0.191(2)	0.437(1)	5.6(7)	C38	0.224(1)	0.133(2)	0.291(1)	10(1)
C26	0.194(1)	0.133(3)	0.412(1)	9(1)	C39	0.245(1)	0.367(3)	0.281(1)	8(1)
C27	0.185(1)	0.371(3)	0.383(1)	9(1)	C40	0.344(1)	0.419(2)	0.318(2)	10(1)
C28	0.284(2)	0.484(3)	0.419(2)	11(1)	O1W	0.3298(8)	0.224(2)	0.201(1)	8.6(7)
C29	0.346(2)	0.299(4)	0.462(2)	13(2)*	O2W	0.247(2)	0.234(3)	0.145(2)	7(1)*
C30	0.291(1)	0.096(3)	0.459(1)	10(1)	C42	−0.039(1)	0.739(2)	0.258(1)	6.7(7)
C31	0.3392(8)	0.217(2)	0.3357(9)	3.7(5)	C41	0.000	0.802(2)	0.250	2.8(6)
C32	0.306(1)	0.133(2)	0.332(1)	6.4(8)					

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

a SQUID susceptometer (905 VTS, SHE Corporation) in the temperature range 2−300 K with an applied magnetic field of 0.1 T. Magnetization measurements for compound **4** were made at 2 K in the magnetic field range 0−6 T. The molar susceptibility was corrected with the diamagnetic contributions (χ_{dia}) of all the atoms by using Pascal's tables and with a temperature independent paramagnetism (χ_{TIP}) from the anions.[18] The EPR spectra were registered in the temperature range 2−300 K with a X-band spectrometer (VARIAN 4500) equipped with a Helium gas flow cryostat.

Results and Discussion

X-ray Crystal Structures: Structure of $[Fe(C_5Me_5)_2]_4$-$[SiMo_{12}O_{40}]$(DMF) (1). From the unit cell parameters and the X-ray powder patterns, we have found that compounds **1**−**3** are isostructural; therefore only the structure of **1** has been determined and is shown in Figure 1. The two independent $Fe(C_5Me_5)_2^+$ moieties stack to form infinite chains along the a direction (Figure 1a) with intrachain Fe−Fe distances of d1 = 7.346(3) Å and d2 = 7.376(3) Å. Six chains fit hexagonal channels along the a direction that incorporate the polyanions and the DMF molecules (Figure 1b). Three types of interchain Fe−Fe distances of 8.349(2), 8.772(3), and 8.806(2) Å are observed. The $[XM_{12}O_{40}]^{-4}$ anion is located at the origin of the unit cell and has the disordered α-Keggin structure.[19]

Structure of $[Fe(C_5Me_5)_2]_4[HFeW_{12}O_{40}]$.$(CH_3CN)\cdot 3H_2O$ (4). Although the crystal structure of the salt **4** is centrosymmetric ($C2/c$ monoclinic space group), the $[FeW_{12}O_{40}]^{5-}$ anion presents the ordered α-Keggin structure with a T_d symmetry.[7] In this case, the W atoms occupy the vertices of a cuboctahedron.[2,19a] In compound **4**, we observe two kinds of W−W distances: one with a mean value of 3.310(1) Å between the W atoms of a W_3O_{13} unit and the other one with a mean value of 3.725(1) Å between the W atoms of adjacent W_3O_{13} units. The Fe central atom is in a tetrahedral position with Fe−O$_t$ average bond lengths of 1.824(2) Å. The other geometrical parameters are in the range of those observed in other Keggin polyanions.[20]

More interesting and unexpected, is the 3-D character of the crystal structure of **4**. The $Fe(C_5Me_5)_2$ cations occupy the vertices of a large irregular cuboctahedron which contains in its cavity the $[FeW_{12}O_{40}]^{5-}$ unit (Figure 2). The W_{12} cuboctahedron and the cationic Fe_{12} cuboctahedron are rotated to each other by a mean angle of 45°. The 3-D structure results from the association of these large $(Fe(C_5Me_5)_2^+)_{12}$ cuboctahedrons by sharing vertices in the a and c directions and by sharing faces in the b direction. As in the W_{12} cuboctahedron, we observe different kinds of Fe−Fe distances between the $Fe(C_5Me_5)_2^+$ cations, although all are longer than 8 Å (see Figure 2b).

Magnetic Measurements. In the temperature range studied (2−300 K) all four compounds obey a Curie−Weiss law $\chi = C/(T - \Theta)$ (see Figure 3) with small negative values of the Curie temperature Θ (from −0.2 K in compound **4** to −4.5 K in compound **2**, see Table 4). These small Θ values are similar to those found in other ferrocenium and decamethylferrocenium complexes[21] and indicate the absence of significant exchange interactions between the organometallic radicals and the inorganic polyanions or among the organometallic radicals. The variation of the μ_{eff} vs T is very similar in all cases (see Figure 4): a constant value is observed between room temperature and ca. 5 K. Below 5 K the μ_{eff} shows a smooth decrease (increase in **1**) (see inset in Figure 4) that may be indicative of weak intermolecular antiferromagnetic exchange interactions at low temperature, as has already been observed in many other salts of ferrocene and its derivatives.[21,22] This anomalous behavior of salt **1** may indicate the presence of intermolecular ferromagnetic exchange interactions at low temperature, although we do not completely exclude the possibility of the existence of ferromagnetic impurities. In compound **4** the decrease in μ_{eff}

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(18) The values of the χ_{TIP} corrections were calculated to eliminate the linear deviations of the χ_mT product at high temperatures from the C value in the $Fe(C_5Me_5)_2^+$ and Bu_4N^+ salts. These χ_{TIP} values are similar to those found in other salts of these polyoxometalates (about 10^{-3} emu·mol^{-1} for compounds **1**−**3** and negligible for compound **4**): see ref 5f.

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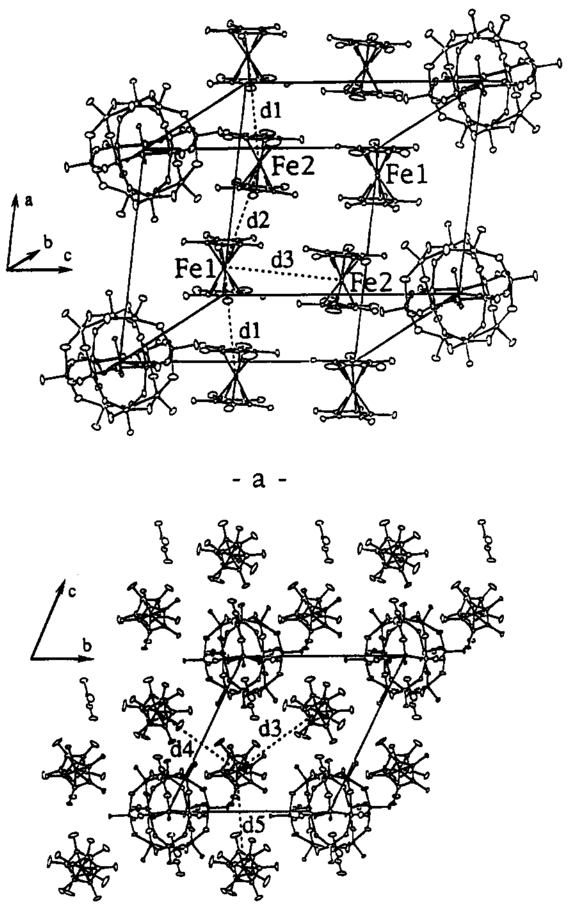
Table 3. Selected Bond Lengths (Å)

(a) $[Fe(C_5(CH_3)_5)_2]_4SiMo_{12}O_{40}[(CH_3)_2NCHO]$			
Mo1−Mo2	3.522(2)	Mo4−Mo5	3.514(2)
Mo3	3.515(1)	Mo6	3.522(3)
Mo5	3.527(2)	O7	1.98(1)
Mo6	3.519(2)	O10	1.82(2)
O1	1.94(1)	O13	1.80(1)
O2	1.81(1)	O14	1.98(2)
O3	1.83(1)	O15	1.66(1)
O4	1.93(1)	Mo5−Mo6	3.520(2)
O5	1.67(1)	O3	1.95(2)
Mo2−Mo3	3.497(2)	O8	1.818(9)
Mo4	3.538(2)	O13	1.950(9)
Mo5	3.529(2)	O16	1.64(1)
O1	1.83(1)	O17	1.81(2)
O6	1.93(2)	Mo6−O4	1.81(1)
O7	1.84(1)	O11	1.97(1)
O8	1.97(1)	O14	1.79(1)
O9	1.652(8)	O17	1.98(1)
Mo3−Mo4	3.517(3)	O18	1.63(2)
Mo6	3.538(2)	Si−O19	1.65(1)
O2	1.97(1)	O20	1.63(2)
O6	1.83(1)	O21	1.60(1)
O10	1.94(1)	O22	1.60(2)
O11	1.82(1)		
O12	1.64(1)		
$Fe(C_5(CH_3)_5)_2$ [a]			
Fe1−C1	2.10(1)	Fe1−C11	2.10(1)
C2	2.08(2)	C12	2.07(2)
C3	2.12(1)	C13	2.06(2)
C4	2.09(1)	C14	2.09(2)
C5	2.08(1)	C15	2.12(1)
$Fe(C_5(CH_3)_5)_2$ [b]			
Fe2−C21	2.10(1)	Fe2−C31	2.09(2)
C22	2.11(2)	C32	2.10(2)
C23	2.10(2)	C33	2.06(1)
C24	2.09(2)	C34	2.12(2)
C25	2.08(1)	C35	2.06(2)
(b) $[Fe(C_5(CH_3)_5)_2]_4$ $HFeW_{12}O_{40}$, $3H_2O$			
W1−W2	3.337(1)	W4−W5	3.716(1)
W2	3.730(1)	Fe1	3.5209(8)
W4	3.304(1)	O2	1.96(1)
W6	3.726(1)	O7	1.93(1)
Fe1	3.507(2)	O10	1.93(1)
O1	1.96(1)	O15	1.92(1)
O2	1.92(1)	O16	1.70(1)
O3	1.95(1)	W5−W6	3.307(1)
O4	1.92(1)	Fe1	3.521(2)
O5	1.70(1)	O6	1.89(1)
W2−W4	3.298(1)	O11	1.94(1)
W6	3.721(1)	O13	1.93(1)
Fe1	3.524(2)	O15	1.92(1)
O1	1.95(1)	O17	1.70(1)
O3	1.91(1)	W6−Fe1	3.5472(8)
O7	1.95(1)	O4	1.92(1)
O8	1.89(1)	O8	1.94(1)
O9	1.73(1)	O11	1.92(1)
W3−W4	3.724(1)	O12	1.95(1)
W5	3.732(1)	O18	1.70(1)
W5	3.308(1)	Fe1−O19	1.82(1)
W6	3.309(1)	O20	1.83(1)
Fe1	3.505(2)		
O6	1.94(1)		
O10	1.88(1)		
O12	1.93(1)		
O13	1.91(1)		
O14	1.69(1)		
$Fe(C_5(CH_3)_5)_2$ [a]			
Fe2−C1	2.11(2)	Fe2−C11	2.09(2)
C2	2.09(2)	C12	2.08(2)
C3	2.09(2)	C13	2.08(3)
C4	2.10(2)	C14	2.09(2)
C5	2.09(2)	C15	2.09(2)
$Fe(C_5(CH_3)_5)_2$ [b]			
Fe3−C21	2.11(3)	Fe3−C31	2.14(2)
C22	2.01(3)	C32	2.09(3)
C23	2.06(3)	C33	2.06(3)
C24	2.06(3)	C34	2.15(3)
C25	2.08(3)	C35	2.07(3)



- a -

- b -

Figure 1. Projection of the structure of **1** down the *ab* and *ac* planes showing: (a) the 1-D stack of $Fe(C_5Me_5)_2^+$ (four anions are omitted for clarity) and (b) The hexagonal channels containing the POM and the DMF molecules: d1 = 7.347(3) Å, d2 = 7.376(1) Å, d3 = 8.773(3) Å, d4 = 8.805(2) Å, and d5 = 8.350(2) Å.

may be due to the zero-field splitting shown by the Fe^{III} in the $[FeW_{12}O_{40}]^{-5}$ polyanion. Thus, the magnetization curve of compound **4** at 2 K indicates that, at least in this salt, there are no magnetic exchange interactions at $T \geq 2$ K (see below).

The μ_{eff} values obtained for all compounds from magnetic and EPR measurements are listed in Table 4. In all cases both values are very close, although the values calculated from the EPR spectra are slightly lower.[23] All the μ_{eff} values per $Fe(C_5Me_5)_2^+$ radical fall within the range of those for other ferrocenium and substituted ferrocenium salts (2.0−2.7 μ_B).[22b] In compounds **1**−**3** these values are very close (2.497, 2.495 and 2.556[24] μ_B, respectively), supporting, thus, that the solid state structure is the same in these three salts. On the other hand, the smaller value (2.295 μ_B)[25] found in the $[FeW_{12}O_{40}]^{5-}$ salt may be due to effects of the anion[26] and/or the fact that this salt presents a 3-D structure, in contrast to the 1-D structure of the other three salts. In the 3-D structure the $Fe(C_5Me_5)_2^+$ units

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(23) The same type of small differences has been found in some biferrocenium salts: see ref 22c.

(24) In this salt $\mu_{eff} = 1.916$ μ_B, corresponding to the $[PMo_{12}O_{40}]^{4-}$ anion, has been subtracted to calculate the contribution of the $Fe(C_5Me_5)_2^+$ radicals. The subtracted value has been deduced from the Bu_4N^+ salt of the corresponding anion and is close to that calculated for the spin only $S = {}^1/_2$ ion: 1.732 μ_B.

(25) In this salt a $\mu_{eff} = 5.834$ μ_B, corresponding to the $[FeW_{12}O_{40}]^{5-}$ anion, has been subtracted to calculate the contribution of the $Fe(C_5Me_5)_2^+$ radicals. The subtracted value has been deduced from the Bu_4N^+ salt of the corresponding anion and is close to that calculated for the spin only $S = {}^5/_2$ ion: 5.916 μ_B.

Table 4. Magnetic Parameters for Compounds **1–4** from EPR and Magnetic Measurements

salt	C	Θ, K	$\mu_{\mathrm{eff}}{}^{a}$	$\mu_{\mathrm{eff}}{}^{b}$	$g_{\parallel}$	$g_{\perp}$	Δg	ζ^{c}	$k'^{\,c}$	$\lvert\xi\rvert^{c}$	$\lvert\delta\rvert^{c}$	ζ^{d}	$k'^{\,d}$	$\lvert\xi\rvert^{d}$	$\lvert\delta\rvert^{d}$
1	3.118	−1.9	2.315	2.497	4.40	1.02	3.38	0.2742	0.6976	283	168	0.2841	0.7093	419	354
2	3.113	−4.5	2.335	2.495	4.35	1.20	3.15	0.3333	0.7343	297	223	0.3733	0.6782	302	203
3	3.727	−3.2	2.315	2.556	4.33	1.16	3.17	0.3196	0.7150	290	206	0.3354	0.6931	286	179
4	6.887	−0.2	2.025	2.295	3.81	0.97	2.84	0.2578	0.5174	210	116	0.3681	0.6758	874	821

[a] μ_{eff} per mole of $\mathrm{Fe(C_5Me_5)_2^+}$ (μ_B units). Calculated from the EPR g factors as $\mu_{\mathrm{eff}} = [(1/3)(g_{\parallel}^2 + 2g_{\perp}^2)S(S+1)]^{1/2}$. [b] μ_{eff} per mole of $\mathrm{Fe(C_5Me_5)_2^+}$ (μ_B units). Measured directly assuming four independent $\mathrm{DMeFc^+}$ molecules and subtracting the contributions of the anions in compounds **3** and **4**. [c] ξ and δ are given in units of cm^{-1}. Parameters obtained from the Maki and Berry equations:[29g] $g_{\parallel} = 2 + 4k'(1 - \zeta^2)/(1 + \zeta^2)$; $g_{\perp} = 4\zeta/(1 + \zeta^2)$, with $\zeta = x/[1 + (1 + x^2)^{1/2}]$, being $x = \delta/\xi$ and $\xi = -k'\xi_0$. We take, as Maki and Berry, $\xi_0 = 405$ cm^{-1}, the value of the free Fe$^{\mathrm{II}}$ ion. [d] ξ and δ are given in units of cm^{-1}. Parameters obtained from the equations of $\chi_{\parallel}$ and $\chi_{\perp}$ derived by Gray et al.:[22b] $\chi_{\parallel} = N\beta^2/kT[(1 + 2k'(1 - \zeta^2)/(1 + \zeta^2))^2 + 16\zeta^2k'^2(kT)/(\xi^2 + \delta^2)^{1/2}(1 + \zeta^2)^2]$, $\chi_{\perp} = N\beta^2/kT[4\zeta^2/(1 + \zeta^2)^2 + (1 - \zeta^2)^2(kT)/(1 + \zeta^2)^2 + (1 - \zeta^2)^2(kT)/(\xi^2 + \delta^2)^{1/2}(1 + \zeta^2)^2]$, $\chi = (\chi_{\parallel} + 2\chi_{\perp}/3$, and $\mu_{\mathrm{eff}} = (8\chi T)^{1/2}$.

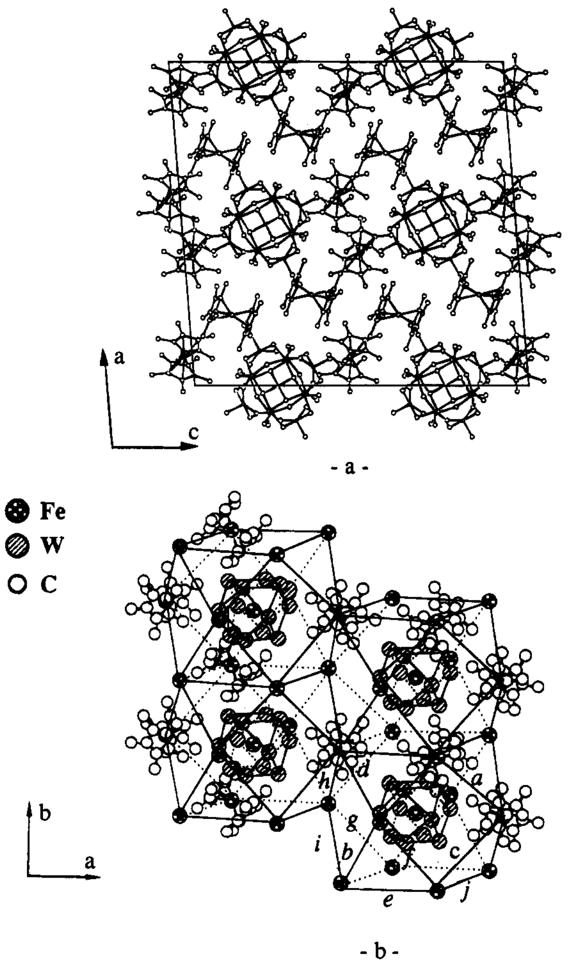

Figure 2. Projection of the structure of **4** down the *ab* and *ac* planes showing (a) the contents of the unit cell and (b) the 3-D packing resulting from the association of the $\mathrm{[Fe(C_5Me_5)_2]_{12}}$ cuboctahedrons sharing vertices along the *a* direction and sharing faces along the *b* direction. For clarity, some $\mathrm{Fe(C_5Me_5)_2^+}$ units and the O atoms of the POM are omitted. $a = 8.026(4)$ Å, $b = 8.382(4)$ Å, $c = 8.574(4)$ Å, $d = 9.013(4)$ Å, $e = f = 9.308(4)$ Å, $g = 9.331(4)$ Å, $h = i = 9.623(4)$ Å, $j = 11.254(4)$ Å.

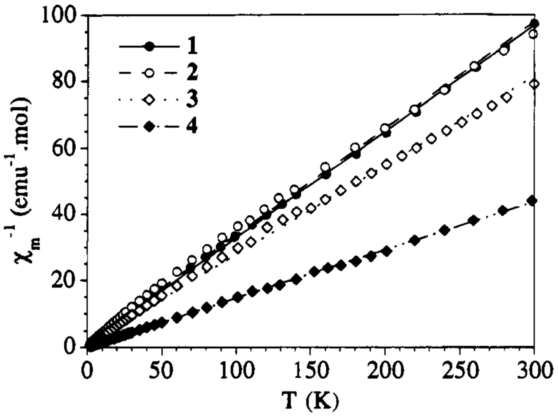

Figure 3. Plot of the inverse of the susceptibility versus temperature for compounds **1–4** at 0.1 T. The solid lines represent the fit to the Curie–Weiss expression (see text).

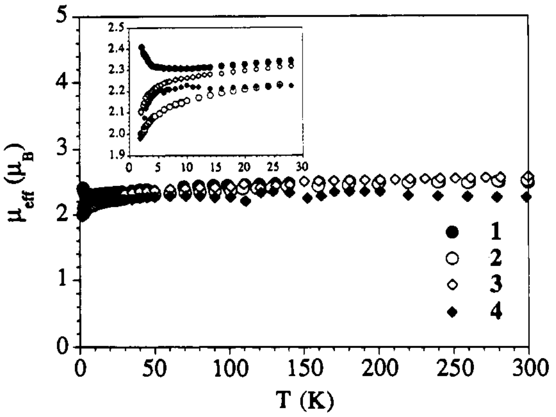

Figure 4. Plot of the effective magnetic moment (μ_{eff}) per mol of $\mathrm{Fe(C_5Me_5)_2^+}$ vs temperature for compounds **1–4** at a magnetic field of 0.1 T. The μ_{eff} values are calculated assuming four independent $\mathrm{Fe(C_5Me_5)_2^+}$ molecules and subtracting the contributions of the anions in compounds **3** and **4**. The low temperature region is shown in the inset.

may present high symmetry distortions, accounting for the decrease in the μ_{eff}. In fact, values of μ_{eff} between 1.99 and 2.31 μ_B have been found in solution for several ferrocenium derivative salts, and have been attributed to distortion effects in the organic radical.[22b] Another possibility is the existence of anisotropic alignments in the microcrystalline samples used for the magnetic measurements. The smaller EPR g values found in compound **4** (see below), the only one with isotropic 3-D distribution of the $\mathrm{Fe(C_5Me_5)_2^+}$ radicals, supports this possibility.

We have performed variable field magnetization measurements on a sample of compound **4** at 2 K with magnetic fields between 0 and 6 T (see Figure 5). The experimental data fit very well to the sum of two independent Brillouin functions,[27] one accounting for the $S = {}^5/_2$ Fe$^{\mathrm{III}}$ from the polyanion and another accounting for the four $S = {}^1/_2$ $\mathrm{Fe(C_5Me_5)_2^+}$ radicals, as it should be expected for two noninteracting systems. With the mentioned S values, the best fit is obtained for g values of 1.992 and 2.539 for the tetrahedral Fe$^{\mathrm{III}}$ and the cationic $\mathrm{Fe(C_5Me_5)_2^+}$, respectively (solid line in Figure 5). These values are

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(26) For some ferrocene salts values of μ_{eff} ranging from 2.34 to 2.62 μ_B have been found, depending on the counterion: (a) Sohn, Y, S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 3233. See also ref. 22b.

(27) Carlin, R. L. *Magnetochemistry;* Springer: Berlin, 1986.

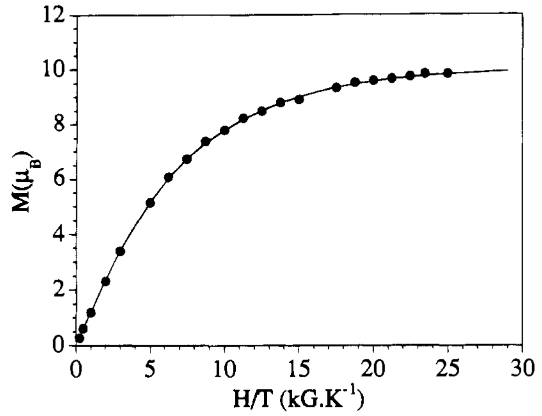

Figure 5. Magnetization versus temperature for compound **4** at T = 2 K. The solid line represents the best fit to the Brillouin expression for two independent systems: the $S = {}^5/_2$ Fe^{III} from the polyanion and the four $S = {}^1/_2$ Fe(C$_5$Me$_5$)$_2^+$ radicals (see text).

similar to those deduced from the susceptibility data (1.972 and 2.650 for the anionic Fe^{III} and the cationic Fe(C$_5$Me$_5$)$_2^+$, respectively).

The absence of significant exchange interactions in all cases may be understood from the X-ray structural data. As mentioned before, salts **1**–**3** present chains of Fe(C$_5$Me$_5$)$_2^+$ radicals with long intra- and interchain Fe–Fe distances (7.346(3) , 7.376(3) Å and 8.350(2), 8.773(3), 8.805(2) Å respectively). Compound **4** shows a different crystallographic structure where the Fe(C$_5$Me$_5$)$_2^+$ radicals are at longer distances (Fe–Fe distances greater than 8 Å), avoiding any direct exchange interaction even at very low temperatures, as shown by the magnetization curve.

EPR Spectra. Although the salts of ferrocenium and its derivatives are EPR silent at room temperature due to a short spin lattice relaxation time T_1,[28] they show a very anisotropic axial signal with $g_\parallel \approx 3.8$–4.4 and $g_\perp \approx 1.2$–1.9 at low temperatures.[29,22c] Figure 6 shows the EPR spectra of powdered samples of compounds **1**–**4** at $T = 4.2$ K. The most important features are as follows: (i) the presence in all spectra, at low temperatures (below approximately 50 K), of two lines at $g_\parallel \approx$ 3.8–4.4 (with $\Delta H \approx 200$–400 G) and $g_\perp \approx 1.0$–1.2 (with ΔH ≈ 1300–3000 G), corresponding to the Fe^{III} in the Fe(C$_5$Me$_5$)$_2^+$ radicals; (ii) The coexistence of these signals with others from the anions in compounds **3** and **4**, confirming the presence of paramagnetic entities also in the inorganic polyanions and the absence of magnetic exchange interactions even at low temperatures.

Compounds **1** and **2** show essentially identical EPR spectra: at temperatures below approximately 50 K both spectra show a characteristic anisotropic signal coming from the Fe(C$_5$Me$_5$)$_2^+$ radicals ($g_\parallel = 4.40$ and $g_\perp = 1.02$ for **1** and $g_\parallel = 4.35$ and $g_\perp = 1.20$ for **2**). At any temperature both compounds show also a weak signal (g = 1.99 with $\Delta H = 110$ G) that does not change significantly with temperature. This feature is probably due to a paramagnetic impurity or decomposition product. Compound **2** presents also a weak signal at low temperatures between the paramagnetic impurity and the $g_\parallel$ signal as well as a shoulder in the signal of $g_\perp$. These features are due to the fact that the samples are microcrystalline and could not be ground sufficiently well to completely average over all crystalline orientations; in fact, the intensity and position of these features change upon rotation of the sample tube.

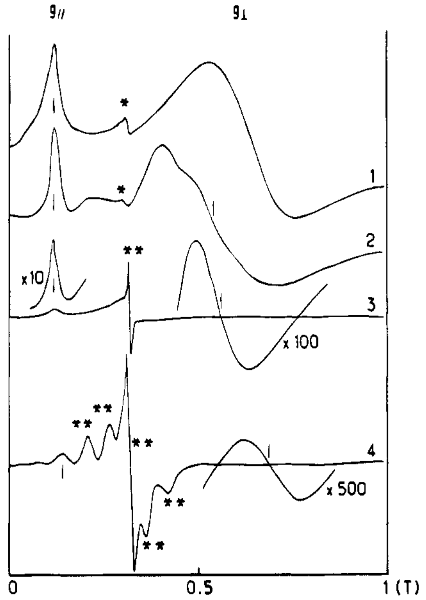

Figure 6. X-band EPR spectra of powdered samples of compounds **1**–**4** at $T = 4.2$ K. In compounds **1** and **2**, * indicates the paramagnetic impurity signal. In compounds **3** and **4**, ** indicates the signals due to the polyanion. $g_\parallel$ and $g_\perp$ indicate the corresponding places of the Fe(C$_5$Me$_5$)$_2^+$ signals.

In compounds **3** and **4** the EPR spectra are more complex but interesting: compound **3** shows, at temperatures below approximately 50 K, the signal of the Fe(C$_5$Me$_5$)$_2^+$ radicals ($g_\parallel = 4.33$ and $g_\perp = 1.16$) and, at any temperature, a single line that varies from $g = 1.97$ with $\Delta H = 1000$ G at room temperature to $g = 1.92$ with $\Delta H = 60$ G at 4.2 K. The variation with temperature of the intensity and line width of this signal is very different from those of the features assigned to paramagnetic impurities in compounds **1** and **2**, so they must be due to the presence of one unpaired electron in the reduced [PMo$_{12}$O$_{40}$]$^{4-}$ anion, in agreement with the 4:1 crystal stoichiometry, the EPR spectrum of the (Bu$_4$N)$_4$[PMo$_{12}$O$_{40}$] salt and the magnetic measurements of compound **3** and the Bu$_4$N$^+$ salt of this anion.[30]

The EPR spectrum of salt **4** presents, at temperatures below approximately 50 K, the signal of the Fe(C$_5$Me$_5$)$_2^+$ radicals ($g_\parallel = 3.81$ and $g_\perp = 0.97$) and, at any temperature, five signals centered around $g \approx 2$ with g values of 2.82, 2.29, 1.97, 1.75, and 1.53 at $T = 4.2$ K. These five characteristics are also

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(28) Fritz, H. P.; Keller, H. J.; Schwarzhans, K. E. *J. Organomet. Chem.* **1967**, *7*, 105.

(29) (a) Duggan, M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955. (b) Morrison, W. H. Jr.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2331. (c) Morrison, W. H. Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998. (d) Prins, R.; Kortbeek, A. G. T. G. *J. Organomet. Chem.* **1971**, *33*, C33. (e) Prins, R. *Mol. Phys.* **1970**, *19*, 603. (f) Prins, R.; Reinders, F. J. *J. Am. Chem. Soc.* **1969**, *91*, 4929. (g) Maki, A. H.; Berry, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 4437. (h) Goan, J. C.; Berg, E.; Podall, H. E. *J. Org. Chem.* **1964**, *29*, 975.

(30) The magnetic measurements of this salt indicate the presence of one extra electron in the Keggin polyanion ($\mu_{\rm eff} = 1.916\ \mu_B$, close to the value of 1.732 μ_B, expected for one unpaired electron). This assignment is also supported by the EPR spectrum of the [PMo$_{12}$O$_{40}$]$^{-4}$ anion that shows a single line at $g \approx 2.0$ that broadens above approximately 80 K. This behavior has been interpreted according to a Robin and Day type class II mixed-valence model, i.e., the unpaired electron is trapped on a Mo atom at low temperatures, but undergoes rapid delocalization among the other Mo atoms as the temperature is raised. We find a similar behavior for the central signal of compound **3**: (a) Bellito, C.; Bonamico, M.; Staulo, G. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 155. (b) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547. (c) Launay, J. P.; Fournier, M.; Sanchez, C.; Livage, J.; Pope, M. T. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 257. (d) Barrows, J. N.; Pope, M. T. In *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Kutal, C., Norton, M. L., Scott, R. A., Eds., Advances in Chemistry Series 226, American Chemical Society: Washington, DC, 1990.

present in the EPR spectrum of the Bu_4N^+ salt of the $[FeW_{12}O_{40}]^{-5}$ anion and show, in both salts, a similar variation of both the g factor and the line width with temperature. They correspond to the high spin $S = {}^5/_2$ tetrahedral Fe^{III} present in the Keggin polyanion and they indicate the existence of a zero field spliting[31] in the $S = {}^5/_2$ Fe^{III} ion. From the spectra at 4.2 K, values of $D = 0.018$ cm^{-1} and $D = 0.024$ cm^{-1} can be estimated for the zero field splinting of the Bu_4N^+ and $Fe(C_5Me_5)_2^+$ salts, respectively,[32] which are in the expected range for this ion, and similar to those found for other high spin Fe^{III} ions.[33] As in salt **3**, in these two salts the presence of any paramagnetic impurity would be completely masked by the central, and more intense signal, at $g \approx 2.0$. Besides all these signals, both $[FeW_{12}O_{40}]^{-5}$ salts show two weak features at g values of approximately 5.9 and 9.8, which correspond to forbidden transitions between levels with $\Delta M_s = \pm 2$.

As can be seen in Table 4, the $g_{\parallel}$ and $g_{\perp}$ values found for compounds **1**−**3** are very similar ($g_{\parallel} = 4.40$, 4.35, and 4.33, and $g_{\perp} = 1.02$, 1.20, and 1.16 respectively). Nevertheless, the values found in salt **4** are considerably smaller ($g_{\parallel} = 3.81$ and $g_{\perp} = 0.97$). This difference is similar to that found for μ_{eff} and is probably due to the same reasons.

Table 4 also lists for compounds **1**−**4** the wave function mixing parameter that results from the departure from the axial symmetry (ζ), the orbital reduction factor (k'), the spin−orbit coupling constant (ξ) and the splitting of the energy levels due to the symmetry distortions (δ). These parameters can be calculated from the EPR values of $g_{\parallel}$ and $g_{\perp}$ by using the equations of Maki and Berry[29g] and from the susceptibility measurements with the equations deduced by Gray et al.[22b]

Although the values deduced for all parameters are within the range of those calculated in other salts of ferrocenium and its derivatives[22,29,34] it is worth commenting on the results obtained for the δ parameter. The δ values found from the EPR spectra at $T = 4.2$ K are similar for the four compounds and close to those observed for the ferrocenium radical (where values of 117, 270, 280, and 322 cm^{-1} have been found, depending on the anion).[29,22c] On the other hand, they are smaller that those observed for other ferrocenium derivatives,[29,22c] indicating weak symmetry distortions in the $Fe(C_5Me_5)_2^+$ radicals. These small distortions may have their origin in the rigidity imposed at low T by the network of these large size polyanions. The δ parameters obtained from the magnetic measurements (for $T > 20$ K) are similar to those obtained from the EPR spectra in the three salts with 1-D structure (**1**−**3**). Thus, even at high temperatures the Keggin polyanions impose their rigidity in the chains of organometallic radicals. On the other hand, at high temperatures the 3-D salt **4** presents a much higher δ value, indicating the presence of significant distortions in the organometallic radicals within the 3-D structure, as already observed in a biferrocenium salt;[22c] i.e., it seems that in salt **4**, at high temperatures, the 3-D lattice of polyanions cannot impose its rigidity as in the 1-D structure. The higher decamethylferrocenium−polyanion distances in this 3-D structure might account for this difference.

Conclusions

In this work, we have seen that it is possible to combine large molecular metal oxide blocks as the polyoxometalates with organometallic radical cations derived from the ferrocene. Thus, we have synthesized and characterized a new family of molecular compounds by mixing decamethylferrocenium and different polyanions with the Keggin structure. This new family presents two different structural types: the first is a 1-D type consisting of chains of the organic radicals with the inorganic polyanions in the tunnels formed by the chains of $Fe(C_5Me_5)_2^+$, whereas in the second one these radicals are disposed in a three dimensional array surrounding the approximately spherical Keggin polyanions. Although in both cases there are not sizable magnetic exchange interactions, both structural types can be very interesting for the search of new molecular ferromagnets. In the first case, the synthesis of tertiary systems by simply adding an acceptor molecule as TCNQ or TCNE could give rise to alternating stacks with a mixed-valence state and ferromagnetic exchange interactions as in $(Fe(C_5Me_5)_2^+)(TCNE^-)$.[21a] The 3-D structure represents a promising system where the introduction of other magnetic polyoxoanions with the Keggin structure having magnetic metals in the surface (substituting the W or Mo atoms) may give rise to magnetic exchange interactions between the organometallic radicals and the polyanions.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations and ORTEP diagrams showing the atomic numbering (19 pages). Ordering information is given on any current masthead page.

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[31] Ingram, D. J. E. *Spectroscopy at Radio and Microwave Frequencies*; Butterworths Scientific Publications Ltd.: London, 1967.

[32] Alger, R. S. *Electron Paramagnetic Resonanc* Interscience Publishers: New York, 1968.

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