Table II. Crystallographic Data for [M(hfacac)$_2$·TCNE]$_x$

	[Cu(hfacac)$_2$·TCNE]$_x$	[Co(hfacac)$_2$·TCNE]$_x$
formula	$CuC_{16}H_2N_4O_4F_{12}$	$CoC_{16}H_2N_4O_4F_{12}$
fw	605.74	601.13
cryst class	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z	2	2
a, Å	6.069 (2)	5.784 (2)
b, Å	20.203 (5)	21.084 (4)
c, Å	8.732 (1)	8.358 (2)
β, deg	90.53 (2)	91.45 (2)
V, Å^3	1070.6 (7)	1019.1 (8)
μ, cm^{-1}	11.53	9.78
ρ_{calc}, g/cm^3	1.879	1.959
T, °C	24	24
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
R_1 (=R^{13})	0.034	0.038
R_2 (=$R_w{}^{13}$)	0.041	0.047

172–174 °C). The anhydrous complex, Co(hfacac)$_2$, is obtained as a fine brown powder by the procedure described for anhydrous Cu(hfacac)$_2$.

[Cu(hfacac)$_2$·TCNE]$_x$. TCNE (30 mg, 23.4 mmol) and anhydrous copper hexafluoroacetylacetonate, Cu(hfacac)$_2$ (56 mg, 11.7 mmol), were placed in a thick-walled glass vessel, and the tube was evacuated on the vacuum line prior to sealing. A significant temperature gradient along the reaction vessel was arranged by allowing half of the tube to protrude outside the heating oven. Lustrous polymeric films and an insoluble black amorphous polymer powder residue remained in the heated area of the tube.[13] Green crystals of [Cu(hfacac)$_2$·TCNE]$_x$ were formed in the cooler regions of the tube. In the melting point apparatus, the green crystals failed to actually melt but instead were transformed to a black amorphous powder at 162 °C. [Cu(hfacac)$_2$·TCNE]$_x$ was characterized by IR spectroscopy (ν_{CN} = 2262, 2252, 2220 cm^{-1}) and by single-crystal X-ray diffraction studies.

[Co(hfacac)$_2$·TCNE]$_x$. Orange crystals of [Co(hfacac)$_2$·TCNE]$_x$ were prepared from TCNE and anhydrous Co(hfacac)$_2$ and characterized in the manner outlined above (ν_{CN} = 2258, 2228, 2214 cm^{-1}).

X-ray Structure Determinations of [M(hfacac)$_2$·TCNE]$_x$. Both compounds crystallize in the monoclinic space group $P2_1/c$ (systematic absences: $0k0$, k = odd; $h0l$, l = odd) with Z = 2. The cell constants were determined from a least-squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) over the range $4 \leq 2\theta \leq 55°$ using the ω–2θ scan technique. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay over the course of data collection. The intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction was performed. Reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement (Table II).

The structures were solved by standard heavy-atom Patterson techniques followed by weighted Fourier syntheses. Hydrogen atoms were found from difference Fourier maps calculated after anisotropic refinement. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

In each compound, the metal atom was found to lie on a crystallographic center of symmetry ($^1/_2$, $^1/_2$, $^1/_2$) and the midpoint of the carbon–carbon double bond in TCNE also lies on a crystallographic symmetry center ($^1/_2$, 0, 1). In both compounds, the CF$_3$ groups exhibited rotational disorder. In the Cu compound, both crystallographically independent CF$_3$ groups were disordered in a 70:30 ratio, while in the Co compound, only one of the two crystallographically independent CF$_3$ groups was disordered, in a 60:40 ratio. The refined positional parameters for selected atoms are found in Table III and IV.

Table III. Refined Positional Parameters of Selected Atoms for [Cu(hfacac)$_2$·TCNE]$_x$

atom	x	y	z	B_{eq},[a] Å^2
Cu	0.5000 (0)	0.5000 (0)	0.5000 (0)	3.229 (9)
O1	0.3345 (3)	0.4264 (1)	0.4142 (2)	3.78 (4)
O2	0.6611 (3)	0.4428 (1)	0.6418 (2)	3.63 (4)
C1	−0.0396 (5)	0.5162 (2)	0.9379 (4)	4.21 (7)
C2	0.0877 (5)	0.5189 (2)	0.7992 (4)	4.28 (7)
C3	−0.2468 (7)	0.5488 (2)	0.9433 (4)	5.9 (1)
N1	0.1939 (5)	0.5196 (2)	0.6952 (3)	5.36 (7)
N2	−0.4124 (7)	0.5741 (2)	0.9548 (5)	9.6 (1)
C4	0.3701 (5)	0.3671 (2)	0.4451 (4)	3.88 (7)
C5	0.5207 (6)	0.3413 (2)	0.5476 (4)	4.74 (8)
C6	0.6533 (5)	0.3810 (2)	0.6379 (4)	3.85 (7)

[a] $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$.

Table IV. Refined Positional Parameters of Selected Atoms for [Co(hfacac)$_2$·TCNE]$_x$

atom	x	y	z	B_{eq},[a] Å^2
Co	0.5000 (0)	0.5000 (0)	0.5000 (0)	2.185 (8)
O1	0.6737 (3)	0.57527 (8)	0.4128 (2)	2.77 (4)
O2	0.3341 (3)	0.55925 (8)	0.6532 (2)	2.76 (4)
C1	1.0385 (5)	0.4844 (1)	0.9354 (3)	2.96 (5)
C2	0.8999 (5)	0.4834 (1)	0.7897 (3)	2.88 (5)
C3	1.2565 (5)	0.4527 (2)	0.9414 (4)	3.65 (6)
N1	0.7781 (4)	0.4848 (1)	0.6818 (3)	3.05 (5)
N2	1.4305 (5)	0.4288 (2)	0.9573 (4)	5.57 (8)
C4	0.6239 (5)	0.6320 (1)	0.4369 (3)	2.90 (5)
C5	0.4625 (6)	0.6560 (1)	0.5407 (4)	3.77 (6)
C6	0.3348 (5)	0.6185 (1)	0.6421 (3)	2.98 (5)

[a] $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha)$.

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Registry No. Cu(hfacac)$_2$, 14781-45-4; Co(hfacac)$_2$, 19648-83-0; [Cu(hfacac)$_2$·TCNE]$_x$, 139070-93-2; [Co(hfacac)$_2$·TCNE]$_x$, 139070-95-4.

Supplementary Material Available: Tables giving structure determination summaries, refined atomic coordinates (with esd's), refined thermal parameters, bond distances, and bond angles for both compounds (11 pages); listings of structure factors (20 pages). Ordering information is given on any current masthead page.

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(12) Attempts to study the black polymeric powders were hindered by its complete insolubility in all organic solvents and even concentrated sulfuric acid. Our observations concerning this poorly characterized polymer are consistent with those reported in previous studies on solid-state reactions between organic tetracyano compounds and metals or metal halides. In particular, diffuse-reflectance infrared spectroscopy has illustrated the disappearance of absorptions due to free –CN groups (at 2220 cm^{-1}) with increased reaction temperature and times and also the corresponding appearance of broad bands covering the region 1260–1380 cm^{-1}, which have been attributed to the phthalocyanine/porphyrazine structure. (See, for example: Wöhrle, D.; et al. *Makromol. Chem.* **1985**, *186*, 2209. Lin, J.; Dudek, L. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1579–1597 and references therein.)

(13) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

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A Simple, Efficient Route to a μ_6-Oxo-Centered Hexanuclear Iron(III) Alkoxide Complex: Preparation and Structure of $Na_2Fe_6O(OCH_3)_{18}{\cdot}6CH_3OH$

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We recently reported the structure of a μ_6-oxo-centered, hexanuclear Fe(III) complex with six entities of fully deprotonated, facially coordinated tris(hydroxymethyl)ethane (THME) entities as chelating ligands.[2] However, the formation of this complex

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Table I. Crystallographic Data for $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_6$

chem formula	$C_{24}H_{78}Fe_6Na_2O_{25}$	fw	1147.94
a, Å	14.367 (3)	space group	$P4_12_12$ (No. 92)
c, Å	24.39 (1)	*T*, °C	22
V, Å^3	5036 (5)	λ, Å	0.71073
Z	4	μ(Mo Kα), cm^{-1}	17.70
$R(F_o)$	0.050	ρ_{calcd}, g·cm^{-3}	1.514
$R_w(F_o)$	0.046		

seemed rather accidental, and no trivial preparation method could be specified. In this note we report a simple and efficient synthetic route and the X-ray structure determination of the corresponding methoxide complex with an almost identical Fe_6O_{19} core.

Experimental Section

Preparation of $Na_2Fe_6O(OCH_3)_{18}·6CH_3OH$. Anhydrous $FeCl_3$ (75 g, Fluka purum) was added in portions to 280 mL of methanol (Fluka puriss. pa), and the resulting suspension was allowed to stand for 24 h. Some undissolved solid was removed from the solution by decantation. A sodium methoxide solution was prepared by adding carefully 28 g of elemental Na to 280 mL of methanol. The dropwise addition of 25 mL of the $FeCl_3$ solution to 75 mL of the sodium methoxide solution resulted in the immediate precipitation of a white solid. An additional 130 mL of methanol was then added. The suspension was allowed to stand for 2 h, and the white solid was filtered out. From the light yellow solution, a large crop of yellowish green crystals were obtained within few days. Both the crystals and the remaining solution are sensitive to atmospheric moisture. Prolonged exposure of the final solution to the laboratory atmosphere obviously resulted in the decomposition of the dissolved compound. A successive change of the color to a deep brown followed by the formation of a brown solid was observed. The crystals were stable even over a period of several months when kept in their mother liquor, but they decayed immediately after the removal of the liquid. The limited stability of the product did not allow the determination of the yield or the realization of elemental analyses. Nevertheless, no particular protection against the uptake of humidity was necessary during the entire preparation procedure.

Crystal Structure Determination. Due to the special behavior of the crystals, the data collection proved to be very difficult. A glass capillary was necessary to protect the crystal in its mother liquor during the measurement. However, the strongly alkaline solution (2 M $NaOCH_3$) attacked every adhesive which was used to seal the capillary tightly. Thus, many tries ended after the determination of the cell constants or the measurement of a few intensities.[3] More success has been achieved with the presence of two bubbles of air between the adhesive and the liquid. In the most successful attempt, about half of the proposed number of intensities could be collected prior to the decay of the crystal. Thus, the data set presented here is still incomplete but sufficiently large to ensure an unambiguous structure determination. The data collection was performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. Three standard reflections were checked at an interval of every 3 h; no significant decrease of intensities was noted until the abrupt decay of the crystal. A total of 2689 intensities were collected by using the $\omega-2\theta$ scan mode; 908 reflections were considered observed with $I \geq 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. Due to the proper crystal dimensions of approximately 0.3 × 0.3 × 0.3 mm and the short lifetime of the crystal, an absorption correction has not been applied. The structure was solved by a combination of Patterson and difference Fourier calculations using SHELXTL PLUS.[4] The positions for 36 hydrogen atoms of the methyl groups were calculated using a riding model with fixed isotropic displacement parameters of 0.08 Å^2. The Fe and O atoms of the Fe_6O_{19} core and the Na atoms were refined with anisotropic displacement parameters; all other non-hydrogen atoms were refined with variable isotropic displacement parameters. The full-matrix least-squares refinement was carried out by minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1$. Neutral scattering factors were those from ref 4. Some structure determination parameters are given in Table I, atom coordinates are listed in Table II, and selected bond lengths and a summary of bond angles are presented in Tables III and IV.

Table II. Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Factors with Estimated Standard Deviations in Parentheses for Non-Hydrogen Atoms of $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_6$

atom[a]	*x*	*y*	*z*	U_{eq}/U_{iso},[b] Å^2
Fe(1)	0.0706 (2)	−0.0867 (2)	0.0003 (1)	0.044 (1)
Fe(2)	0.0727 (3)	0.0704 (3)	0.0942 (1)	0.048 (1)
Fe(3)	0.2301 (2)	0.0715 (3)	0.0003 (1)	0.052 (1)
Na(1)	0.2389 (8)	−0.0989 (8)	−0.1000 (4)	0.091 (3)
O(1)	−0.067 (1)	−0.067 (1)	0	0.040 (3)
O(2)	0.2100 (9)	−0.067 (1)	−0.0019 (6)	0.061 (4)
O(3)	0.079 (1)	−0.217 (1)	−0.0059 (7)	0.074 (4)
O(4)	0.072 (1)	−0.065 (1)	0.0794 (4)	0.055 (4)
O(5)	−0.067 (1)	0.075 (1)	0.0822 (4)	0.049 (3)
O(6)	0.209 (1)	0.069 (2)	0.0825 (6)	0.072 (4)
O(7)	0.065 (1)	0.080 (1)	0.1703 (4)	0.083 (4)
O(8)	0.070 (1)	0.070 (1)	0	0.046 (3)
O(9)	0.208 (1)	0.208 (1)	0	0.075 (4)
O(10)	0.069 (1)	0.210 (1)	0.0816 (5)	0.054 (4)
O(11)	0.358 (1)	0.059 (2)	−0.0044 (8)	0.092 (4)
C(1)	−0.138 (1)	−0.138 (1)	0	0.074 (7)
C(2)	0.271 (2)	−0.121 (2)	0.0322 (8)	0.075 (6)
C(3)	0.036 (2)	−0.297 (2)	0.021 (1)	0.127 (7)
C(4)	0.074 (2)	−0.133 (1)	0.1224 (8)	0.091 (7)
C(5)	−0.122 (2)	0.016 (2)	0.1162 (9)	0.080 (6)
C(6)	0.282 (2)	0.061 (2)	0.122 (1)	0.147 (8)
C(7)	0.114 (2)	0.063 (2)	0.217 (1)	0.151 (8)
C(9)	0.273 (2)	0.273 (2)	0	0.119 (8)
C(10)	0.125 (2)	0.269 (2)	0.1146 (8)	0.065 (5)
C(11)	0.429 (2)	0.106 (2)	0.015 (1)	0.139 (7)
O(12)	0.208 (2)	−0.067 (2)	−0.1909 (8)	0.138 (6)
O(13)	0.395 (2)	−0.067 (2)	−0.0768 (9)	0.142 (6)
O(14)	0.204 (2)	−0.252 (2)	−0.082 (1)	0.139 (7)
C(12)	0.259 (2)	−0.058 (3)	−0.235 (1)	0.217 (8)
C(13)	0.473 (2)	−0.066 (3)	−0.105 (1)	0.174 (8)
C(14)	0.229 (3)	−0.332 (2)	−0.086 (2)	0.194 (8)

[a] The coordinates of the 26 additional symmetry-related atoms are obtained according to ref 6. [b] The atoms C(1)–C(14) and O(12)–O(14) were refined isotropically. $U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

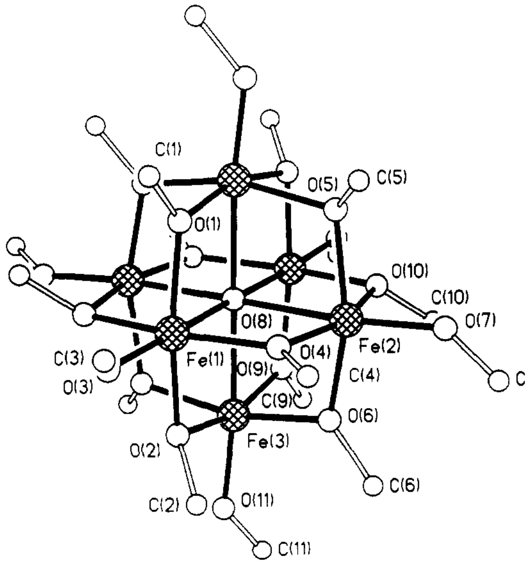

Figure 1. Structure of the $[OFe_6(OCH_3)_{18}]^{2-}$ complex with numbering scheme. For the unlabeled atoms, see ref 6.

Results and Discussion

The molecular architecture of polynuclear Fe(III) complexes has repeatedly fascinated chemists.[5] The Fe_9O_{16} core as found

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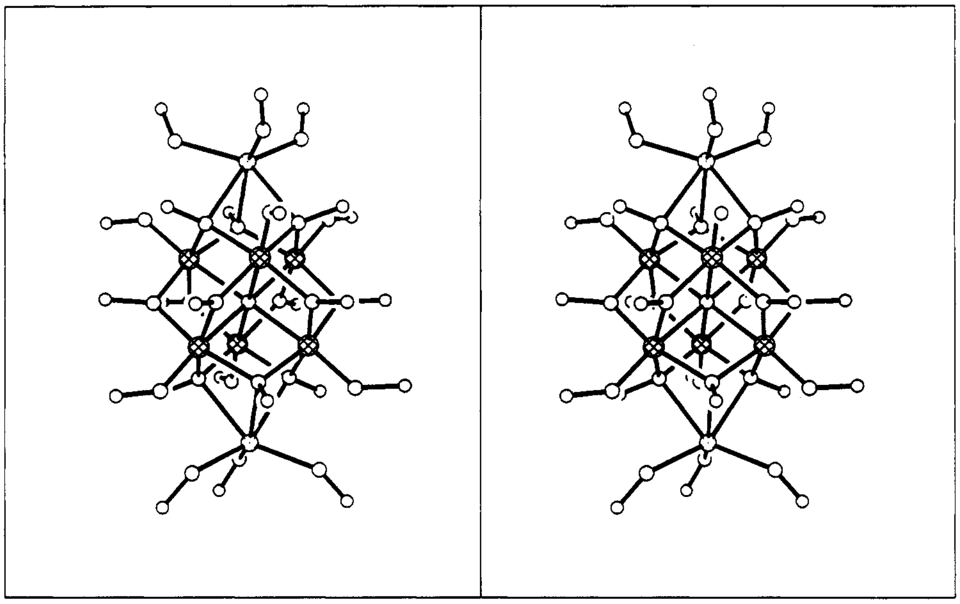

Figure 2. Stereoview of the entire $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_6$ molecule.

Table III. Selected Bond Lengths (Å) of $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_6$ with Estimated Standard Deviations in Parentheses

Fe(1)–Fe(1′)	3.196 (4)	Fe(1)–Fe(2)	3.216 (5)
Fe(1)–Fe(2′)	3.250 (5)	Fe(1)–Fe(3)	3.228 (5)
Fe(2)–Fe(3)	3.219 (5)	Fe(2)–Fe(3′)	3.253 (5)
Fe(3)–Fe(3′)	3.223 (5)	O(1)–Fe(1)	1.99 (1)
O(2)–Fe(1)	2.02 (1)	O(2)–Fe(3)	2.02 (2)
O(3)–Fe(1)	1.88 (2)	O(4)–Fe(1)	1.96 (1)
O(4)–Fe(2)	1.98 (2)	O(5)–Fe(1′)	2.03 (1)
O(5)–Fe(2)	2.02 (2)	O(6)–Fe(2)	1.98 (1)
O(6)–Fe(3)	2.03 (1)	O(7)–Fe(2)	1.87 (1)
O(8)–Fe(1)	2.26 (2)	O(8)–Fe(2)	2.298 (7)
O(8)–Fe(3)	2.30 (2)	O(9)–Fe(3)	1.98 (1)
O(10)–Fe(2)	2.02 (2)	O(10)–Fe(3′)	2.02 (1)
O(11)–Fe(3)	1.85 (2)	Na(1)–O(2)	2.47 (2)
Na(1)–O(5′)	2.44 (2)	Na(1)–O(10′)	2.48 (2)
Na(1)–O(12)	2.31 (2)	Na(1)–O(13)	2.35 (2)
Na(1)–O(14)	2.30 (3)		

Table IV. Summarized Bond Angles (deg) of $[OFe_6(OCH_3)_{18}]^{2-}$

type of angle[a]	no.	range	av value
fac-Fe–Fe–Fe	24	59.2–60.9	60.0
mer-Fe–Fe–Fe	12	89.4–90.6	90.0
trans-Fe–O(8)–Fe	3	178.6–179.4	179.1
cis-Fe–O(8)–Fe	12	88.9–91.1	90.0
$Fe–O_{br}–Fe$	12	106.2–109.8	107.4
$O(8)–Fe–O_t$	6	172.9–173.9	173.6
$O(8)–Fe–O_{br}$	24	79.4–82.7	81.3
$O_t–Fe–O_{br}$	24	92.5–105.0	98.6
cis-$O_{br}–Fe–O_{br}$	24	85.3–90.9	88.7
trans-$O_{br}–Fe–O_{br}$	12	160.5–163.7	162.5

[a] br = bridging; t = terminal.

Table V. Characteristic Interatomic Distances (Å) in the Fe_6O_{19} Cores of $[OFe_6(OCH_3)_{18}]^{2-}$ and $[OFe_6(THME)_6]^{2-}$

	$[OFe_6(OCH_3)_{18}]^{2-}$		$[OFe_6(THME)_6]^{2-}$	
	range	av value	range	av value
$Fe–O_{cent}$	2.25–2.30	2.29	2.23–2.27	2.25
$Fe–O_{br}$	1.95–2.03	2.00	1.99–2.03	2.01
$Fe–O_t$	1.85–1.88	1.86	1.86–1.89	1.88
Fe–Fe	3.20–3.25	3.23	3.16–3.23	3.19

previously in $[OFe_6(THME)_6]^{2-}$ and in the present $[OFe_6(OCH_3)_{18}]^{2-}$ is remarkable in this respect considering its idealized O_h symmetry[6] and the high coordination number of the central oxygen atom.[7] In the $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_3$ molecule, this central oxygen atom is approximately in the center of an octahedron formed by the six Fe(III) atoms. The iron atoms themselves are linked to each other by twelve μ_2-methoxide bridges. A distorted octahedral coordination sphere of the ferric ions is completed by six terminal methoxide ligands (Figure 1). Each of the two Na^+ ions, required for charge balance, is bound to three methoxide bridges of the $OFe_6(OCH_3)_6$ moiety and to three additional methanol molecules leading to an idealized C_3-coordination geometry ($CN_{Na} = 6$). A stereoview of the entire $OFe_6(OCH_3)_{18}Na_2(HOCH_3)_6$ molecule is presented in Figure 2. All of the 24 methyl groups are located on the periphery of the molecule, generating a hydrophobic surface and making the compound soluble in nonpolar solvents. Although the Fe_6O_{19} cores in $[OFe_6(OCH_3)_{18}]^{2-}$ and $[OFe_6(THME)_6]^{2-}$ are essentially the same, the slightly shorter $Fe–O_{cent}$ and Fe–Fe distances in the THME complex suggested that the polydentate THME acted as a clamp which holds the core together more tightly (Table V). Accordingly the THME complex is more resistant to hydrolysis.

Polynuclear, oxo-centered metal compounds with alkoxides as bridging and terminal ligands are well established in coordination chemistry. The complexes of a variety of metals including Ti,[8a] Zr,[8b] Y,[8c,8d] Mo,[8e] Ce,[8f] and U[8g] have been structurally characterized. However, as far as we know, $[OFe_6(THME)_6]^{2-}$ and $[OFe_6(OCH_3)_{18}]^{2-}$ are the first two representatives of iron(III). If we take into account that the same Fe_6O_{19} core is formed in two complexes, obtained by different synthetic procedures,[9] it seems possible that this core represents a general structure type for iron (III) alkoxide complexes formed in alkaline alcoholic media with a low water content. Thus, the difference between the alkaline iron(III)–methanol and iron(III)–water system is quite

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(6) The crystallographic symmetry of the $OFe_6(OCH_3)_{18}Na_2(CH_3OH)_6$ molecule is C_2. The atoms C(1), O(1), O(8), O(9), and C(9) are located on the 2-fold axis. All other atoms are duplicated by the symmetry operation *y*, *x*, –*z*.

(7) Obviously, the amount of water in the commercially available methanol (0.05% = 0.02 M) was sufficient to serve as a source for the central oxygen atom.

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(9) $[OFe_6(OCH_3)_{18}]^{2-}$: one-pot-synthesis. $[OFe_6(THME)_6]^{2-}$: hydrolysis of a precursor, obtained in dry NEt_4OCH_3/methanol.

remarkable. No low molecular weight complexes of the type $[Fe_xO_y(OH)_z]^{3x-2y-z}$ have been isolated from aqueous media. In strongly alkaline aqueous solutions, Fe(III) exists either as solid FeO(OH) or as mononuclear $[Fe(OH)_4]^-$.[10] Also, in aqueous ethanediol, glycerol, or sorbitol solutions, the formation of mononuclear complexes has been observed at concentrations of $OH^- \geq 1$ M and polynuclear species have only been found at much lower base concentration.[11]

Acknowledgment. We thank Prof. Walter Schneider for support and discussions.

Registry No. $Na_2Fe_6O(OCH_3)_{18}\cdot6CH_3OH$, 139494-73-8.

Supplementary Material Available: Tables SI–SV, listing crystallographic data, anisotropic displacement parameters, positional parameters of the hydrogen atoms, and interatomic distances and bond angles (8 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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A Novel and Generalized Approach to the Synthesis of ML_3^{n+} [M = Ru(II), Rh(III); L = 2,2′-Bipyridine, 1,10-Phenanthroline, 2-(Arylazo)pyridine; *n* = 2, 3]

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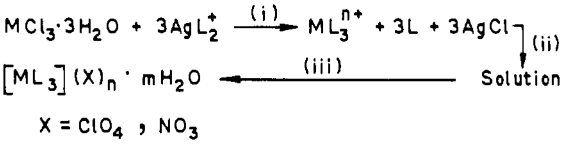
Introduction

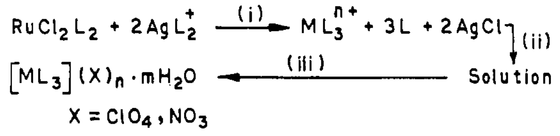
The chemistry of tris(2,2′-bipyridine)ruthenium(II) and -rhodium(III) complexes and complexes of related ligands has had an extensive literature[1–5] in recent years. The reason for this is primarily the relevance of this chemistry to photophysical, photochemical, and redox phenomena. But until now, no simple and general synthetic route has been available for the synthesis of such compounds. For example, the tris complex of 2,2′-bipyridine (L^1) is commonly synthesized[6] by fusion of MCl_3 with the ligand at a very high temperature, whereas the syntheses of the tris complexes of 1,10-phenanthroline[7] (L^2) and 2-(*m*-tolylazo)pyridine[8] (L^3) involve several steps which need extra purification at every stage to eliminate contaminated products. The standard reported synthetic routes are not only lengthy but also cumbersome, and in most of the cases the routes are inefficient. Therefore, there is an obvious need to develop new and direct procedures, of general application, for the synthesis of the important title compounds. In the present report, we describe high-yield, single-pot, and general synthetic routes to ML_3^{n+} from either hydrated MCl_3 or MCl_2L_2 [M = Ru(II), Rh(III); L = L^1–L^3] and the silver bis complex of the corresponding ligand.

Scheme I[a]



[a] Key: (i) MeOH, heat; (ii) filtration; (iii) aqueous solution of $NaClO_4$ or $NaNO_3$.

Scheme II[a]



[a] Key: (i) MeOH, heat; (ii) filtration; (iii) aqueous solution of $NaClO_4$ or $NaNO_3$.

Results and Discussion

The synthetic reactions are shown in Schemes I and II. In Scheme I, we describe the one-pot facile synthetic route to ML_3^{n+} from hydrated MCl_3 using AgL_2^+[9–11] as a synthon. The primary reaction involving hydrated MCl_3 and AgL_2^+ is carried out in boiling methanol in a 1:3 proportion to yield directly ML_3^{n+}, excess L, and insoluble AgCl. The cationic complex, ML_3^{n+}, has been isolated as either its perchlorate hydrate or its nitrate hydrate salt from solution.[12] Recrystallization, either from water or from a methanol–water mixture, yields a highly crystalline product. In the case of ruthenium, the yield lies in the range 65–70% whereas the yield of $[Rh(L^1)_3](ClO_4)_3\cdot H_2O$ is 55%. The direct synthesis of ML_3^{n+} from $MCl_3\cdot3H_2O$, as evidenced by Scheme I, requires complete substitution of 3 mol of Cl^- by 3 mol of L. Thus, it was logically anticipated that the interaction of hydrated MCl_3 with $[AgL_2]^+$ in a 1:3 proportion might lead directly to the desired product. Accordingly, in line with the synthetic strategy, the reactions stated in the scheme were undertaken; they proceeded smoothly to yield $[ML_3](X)_n\cdot mH_2O$ [M = Ru(II), Rh(III); L = L^1–L^3; X = ClO_4, NO_3; *n* = 1, 3; *m* = 1, 2, 6] in a high yield.[13] In the case of ruthenium, it is believed that the reduction of ruthenium(III) to ruthenium(II) is accomplished[14] by the reducing

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(12) Excess L can be recovered from the reaction mixture (see Experimental Section).

(13) In the case of L^2, the reaction is relatively slow and the yields are also low. This is probably due to lesser solubility of $[Ag(L^2)_2]^+$ complexes in methanol. The reaction of hydrated $RhCl_3$ and $[Ag(L^3)_2]^+$, instead of yielding a tris complex, yields a mixture of compounds. Indications are strong that the reaction directly produces a Rh(I) bis-chelated compound as the major product. Isolation and characterization of the product are underway.

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