Inorg. Chem. 1990, 29, 2883–2885

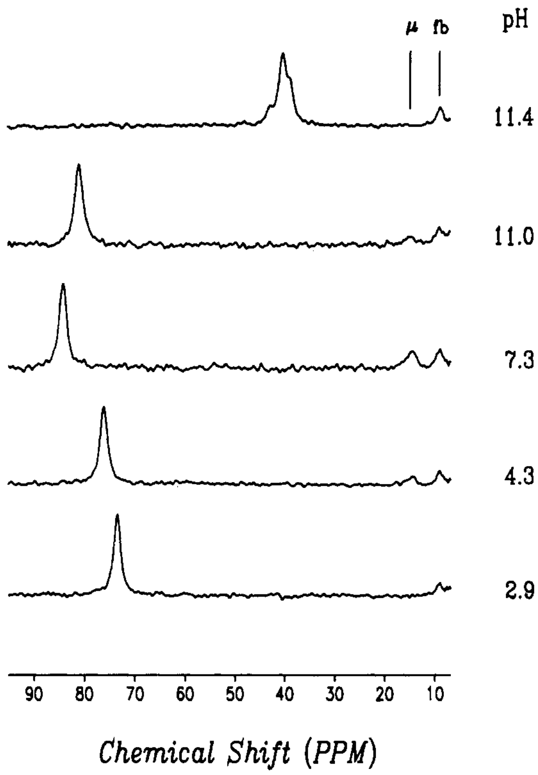

Figure 4. ^{2}H NMR spectra of 1 mM $Fe^{III}(T(2\text{-}N\text{-}Me)PyP)^{5+}(aq)$ solutions (in 0.2 M $NaClO_4$) at pH 2.9, 4.3, 7.3, 11.0, and 11.4, acquired at 38 MHz in a 10-mm tube at ambient temperatures. The spectra contained 8K data points over a spectral window of 10 kHz. Solution pH was adjusted by adding either NaOH or $HClO_4$. Minor contributions from free base (fb) and iron μ-oxo dimer (μ) are indicated.

frequencies are characteristic of high- and low-spin Fe^{III} species,[12] respectively. The ESR spectrum (Figure 3) is characteristic of a high-spin Fe^{III} (g = 6 and 2) species until the titration approaches the second equivalence point. Low-spin features then appear in the spectrum and beyond pH 11. The spectrum indicates nearly all low-spin Fe^{III} ($g_z = 2.54$, $g_y = 2.15$, $g_x = 1.90$) at 120 K.[15] ^{2}H NMR spectra of the β-deuterated pyrrole complex (Figure 4) show a resonance shifting from 73.5 ppm at pH 2.9 to 84 ppm at pH 7.3, indicating conversion from one high-spin Fe^{III} species to another,[16] while at pH 11.4 the resonance is a multiplet between the high-spin values and a typical low-spin value (−20 to −30 ppm).[16] Curie plots for these signals exhibit a negative slope and are consistent with a spin equilibrium at pH 11.4. Likewise, the RR spectrum at this pH shows both low- and high-spin porphyrin marker bands. The low-spin ESR spectrum (Figure 3), taken at 120 K, reflects the low-spin character of the ground state at this temperature.

These data are consistent with previous spectrophotometric titrations of this complex,[6,7] which indicate pK_a values of ~5 and ~11. Kobayashi[6] had similarly inferred high-spin character for the acid and neutral species, assigned to the aquo- and mono(hydroxo) complexes, respectively, and low-spin character for the high-pH complex, assigned to the bis(hydroxide). Our data indicate that the latter species constitutes a spin-state equilibrium at room temperature. The assignment of the 443-cm^{-1} Fe-OH stretch to the low-spin component of this mixture is based on the observation that this band persists at low temperature (data not shown).

The 27-cm^{-1} ^{18}O downshift of the 541-cm^{-1} mono(hydroxo) band (Figure 1) is as expected for an Fe–OH oscillator, but the 13-cm^{-1} upshift in D_2O is surprising; an 11-cm^{-1} downshift would be expected on the basis of a diatom calculation with point mass 17 (OH) and 18 (OD) oscillators. A similar upshift has been noted in hemerythrin,[17] however, and was attributed to coupling with the Fe–O–H bending mode. We have been able to model the upshift with a bent (110°) Fe–O–H oscillator having Fe–O and O–H stretching force constants of 2.3 and 5.13 mdyn/Å, a bending force constant of 0.2 mdyn Å/rad^2 and a stretch–bend interaction constant of 0.07 mdyn/Å.[18] The bending mode is calculated to be 614 cm^{-1} for Fe–OH and 437 cm^{-1} for Fe–OD, thus crossing over the Fe–OH stretch and producing the upshift via kinematic coupling.

The stretching frequency is higher for the high-spin mono(hydroxo) than the low-spin bis(hydroxide) complex. Part of this effect arises from altered kinematics, as the bis(hydroxide) stretching mode is the symmetric stretch in which the central Fe atom does not move, but part of it stems from a higher force constant for the mono(hydroxo) complex. A linear triatom calculation with point mass OH ligands gives a stretching force constant of 2.0 mdyn/Å for the bis(hydroxide) complex. This value is quite reasonable for low-spin Fe^{III}. For comparison, the force constant is 1.6 mdyn/Å for the bis(imidazole) adducts of both Fe^{III} and Fe^{II} porphyrins.[19] Why then is the mono(hydroxo) force constant even larger, 2.3 mdyn/Å, despite the Fe^{III} being high-spin? The answer may lie in the ability of the single hydroxide ligand to polarize the iron orbitals. High-spin Fe^{III} has a half-occupied d_{z^2} orbital, which is formally antibonding with respect to the axial ligand. The d_{z^2} electron can, however, be concentrated on the back side of the 5-coordinate complex, via $3d_{z^2}$–$4p_z$ hybridization. This permits the hydroxide σ electrons unimpeded access to the Fe^{III} ion, and in addition, the hydroxide π electrons can engage in donor interactions with the filled Fe^{III} d_π orbitals. Strong bonding in high-spin 5-coordinate Fe^{III} adducts finds precedence in the case of the fluoride[3,20] and methoxide[21] complexes.[22] These arguments imply that the aqueous mono(hydroxo) complex is predominantly five-coordinate and that a water molecule is at most loosely bound as a sixth ligand.

The RR, NMR, and ESR data provide consistent and compelling evidence for the existence of primarily three coordination states of the $Fe(T(2\text{-}N\text{-}Me)PyP)^{5+}(aq)$ ion in solutions of varying pH: a high-spin aquo complex at low pH, a high-spin 5-coordinate mono(hydroxo) complex at intermediate pH, and a high-spin/low-spin equilibrium of bis(hydroxide) species at high pH.

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Soluble and Volatile Yttrium and Copper Alkoxo–Acetylacetonato Derivatives. Synthesis and Crystal Structure of $Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4$

The synthesis of high-tech materials by chemical routes such as sol–gel technology[1] or chemical vapor-phase decomposition[2] is increasingly used as an approach to overcoming some of the limits of the conventional solid-state synthesis. Yttrium is involved as oxide in various materials such as yttrium–iron garnets (YIG), in high T_c superconductors, and in the stabilization of thermomechanical ceramics.[3] Alkoxides and related compounds display a number of attractive features that make them good candidates for precursors of oxides via chemical routes.

We recently reported the synthesis and molecular structure of tris(2-methoxyethanolato)yttrium (**1**).[4] Its remarkable solubility is attractive for sol–gel applications; however, its poor volatility due to its decameric character as a crown precludes its use for MOCVD techniques. High T_c superconductors to be used in microelectronic devices need to be able to carry high critical currents; only $YBa_2Cu_3O_{7-x}$ coatings grown by MOCVD techniques appear so far to meet these requirements, and novel volatile precursors are desirable.

Heterometallic species are particularly attractive since they would allow reduction of the number of precursors and thus of the parameters to be controlled during the deposition process. An attractive entry into such complexes was envisioned as the combination of alkoxides and β-diketonates. This expectation was not fulfilled, and reaction between $[Y(OC_2H_4OMe)_3]_{10}$ and $Cu(acac)_2$ offered homometallic products resulting from ligand redistribution reaction as the most stable derivatives. Thus we now wish to report the synthesis and molecular structure of a new yttrium precursor, $Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4$ (acacH = $C_5H_8O_2$, acetylacetone). The copper derivative $Cu(OC_2H_4OMe)(acac)$, obtained during the reaction, represents one of the few soluble copper(II) alkoxide derivatives.

Reactions between alkoxides and β-diketonates of different metals might be a way to construct heterometallic species as well as to form heteroleptic homometallic species.[5] The reaction between $[Y(OC_2H_4OMe)_3]_{10}$ and $Cu(acac)_2$ (1:3 ratio) at room temperature over 5 h offered several products (eq 1). Extraction

$$[Y(OC_2H_4OMe)_3]_{10} + 30Cu(acac)_2 \rightarrow 3Y_3(OC_2H_4OMe)_5(acac)_4 + [Cu(OC_2H_4OMe)(acac)]_m + \cdots \quad (1)$$

of the reaction mixture by petroleum ether and concentration of the solution gave white crystals of **2**.[6] The IR spectrum of this diamagnetic material showed the absorption bands characteristic of acetylacetonato groups, especially at 1607 cm^{-1} (ν_{as}(C=O)). Further concentration offered a blue paramagnetic derivative analyzing as $Cu(OC_2H_4OMe)(acac)$ (**3**) (ν_{as}(C=O): 1587, 1518 cm^{-1}). Although its structure has not been determined, it is probably a tetramer, as observed for $[Cu(\mu\text{-}OC_2H_4O^iPr)(acac)]_4$.[7]

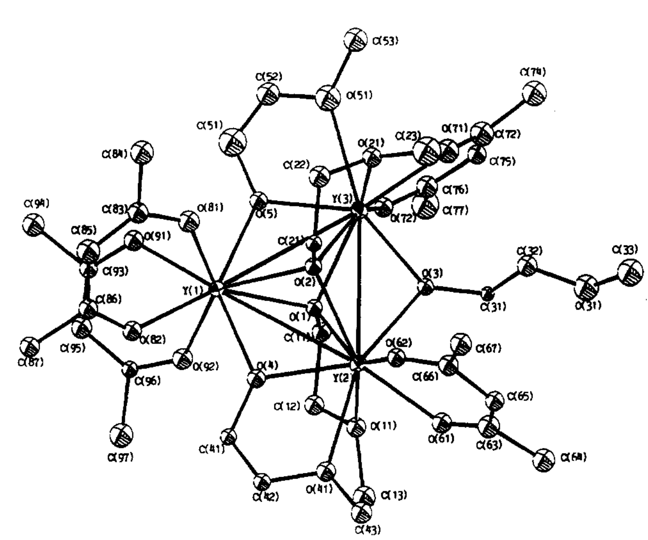

Figure 1. ORTEP drawing of $Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4$ (**2**) omitting hydrogens. Selected structural parameters (bond lengths, Å): Y–μ_3OR, 2.47 av; Y–μ_2-OR, 2.26 av; Y–O(Me), 2.545 av; Y–O(acac), 2.304 av; Y---Y, 3.551 av.

An X-ray structure determination[8] of the white crystals **2** shows it to be a trinuclear yttrium heteroleptic species, $Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4$. An ORTEP plot is shown in Figure 1, with important bond distances and angles. The three metal atoms form a nearly regular Y---Y (3.551 Å$_{av}$) triangle, capped above and below by a triply bridging chelating methoxyethoxide group. The different metals are also linked to each other by two bridging–chelating alkoxide moieties and by a bridging alkoxide in which the ether functionality remains uncoordinated (Y---OMe: 5.35 Å). All yttrium atoms are octacoordinated, the overall coordination polyhedron being achieved by classical bidentate acetylacetonato ligands. The molecule has a pseudo-C_2 axis that contains Y1 and O3. The overall structure is related to that of $Y_3(\mu_3\text{-}O^tBu)(\mu_3\text{-}Cl)(\mu\text{-}O^tBu)_3(O^tBu)_4(THF)_2$,[12] although the ether functionality of the OC_2H_4OMe groups and the β-diketonate ligands allow the metal to attain a higher coordination number.

Three different coordination modes of the 2-methoxyethoxide moieties are thus present in a single molecule. Both the doubly bridging–chelating and the nonchelating mode have been observed recently in this laboratory for $[Y(OC_2H_4OMe)_3]_{10}$[4] and [Bi$_2$-

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(8) **2** crystallizes in the space group $P2_1/n$, with the following unit cell parameters: a = 15.981 (3) Å, b = 10.637 (3) Å, c = 27.427 (4) Å, β = 98.39 (3)°, V = 4612.62 Å^3, Z = 4; D_c = 1.501 g.cm^{-3}, and μ(Mo Kα) = 38.30 cm^{-1}. A total of 4856 ($3 < 2\theta < 40°$) data were collected at room temperature (20 °C) on a Nonius CAD4 diffractometer. Yttrium atoms were found by using SHELXS.[9] All remaining non-hydrogen atoms were located on successive difference electron density maps. The structure was refined by least-squares techniques with approximation (in three blocks) to the normal matrix using CRYSTALS.[10] A total of 1283 reflections with $I > 3\sigma(I)$, were used to refine the structure: R = 0.0532, R_w = 0.0624, for 241 variables. In view of the low number of reflections used, only Y atoms were refined anisotropically. H atoms were placed in calculated positions. Their coordinates were not refined but recalculated after each cycle. They were assigned isotropic temperature factors 20% higher than those of the carbon atoms to which they were attached. Anomalous dispersion terms were applied. Empirical absorption correction using DIFABS[11] was performed. Complete crystallographic details are included in the Supplementary Material.
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$(OC_2H_4OMe)_6]_\infty$,[13] respectively. The triply bridging chelating coordination mode has been found in the tetranuclear cluster $Ba_2Cu_2(OC_2H_4OMe)_4(acac)_4 \cdot 2OHC_2H_4OMe$.[5] The Y–O alkoxide bond distances are significantly longer for the μ_3 moieties than for those of μ_2 (2.44 (2)–2.50 (2) Å vs 2.28 Å av), and longer than those observed for terminal methylmethoxide groups.[4] The Y–O bond lengths involving the ether functionality are quite long (2.52 (2)–2.57 (2) Å). The μ_3-oxygen atoms are clearly pyramidal (sum of the Y–O–Y angles is 285.3° average), and located at 1.230 and 1.287 Å above and below the Y_3 planes, respectively. The Y–O(acac) distances (2.25 (2)–2.35 (2) Å) are comparable to those reported in the literature.[14] These results show the preference of the 2-methoxyethoxide groups over the acetylacetonate ones to act as bridging ligands.

$Y_3(\mu_3,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^2\text{-}OC_2H_4OMe)_2(\mu_2,\eta^1\text{-}OC_2H_4OMe)(acac)_4$ (**2**) displays a complex behavior in solution, and several molecular species are observed in $CDCl_3$ solution for instance, as evidenced by ^1H and ^{13}C NMR. Several hypotheses such as a nonchelating behavior of some μ_3 or μ_2 groups could account for the spectroscopic observations, but detailed analysis has not been carried out. By contrast to $Y_2(OAc)_2(acac)_4(H_2O)_2$,[14] no free acetylactone was detected in solution.

The nature of the isolated yttrium and copper products appears to be independent of the stoichiometry of the reaction and/or the solvents used (toluene, pentane, additional methoxyethanol). While the method explored here yielded no isolable mixed-metal Y/Cu compounds, the intermediacy of such a derivative(s) is implicit in the synthetic reaction (eq 1). Indeed, no reaction proceeds between $Cu(acac)_2$ and anhydrous 2-methoxyethanol under similar conditions. These results also suggest that ligand metathesis can be a complicating factor in building multimetallic systems.

Direct reaction between **1** and acacH (1:9 molar ratio) in toluene offers an alternative route to **2**. This novel yttrium precursor displays a volatility and a thermal stability (as established by thermal gravimetric analysis) comparable to that of $[Y(acac)_3]_m$, although the presence of the functional alkoxide ligands reduces its sensitivity to moisture. The copper acetylacetonate alkoxide **3** is highly soluble as well as hydrolyzable, while the homoleptic Cu(II) parent alkoxide $[Cu(OC_2H_4OMe)_2]_m$ is polymeric and insoluble.[15] It is therefore an attractive precursor for sol–gel applications, and further experiments are in progress.

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Supplementary Material Available: Tables of a full summary of the crystallographic data, positional and isotropic thermal parameters, anisotropic thermal parameters, positional parameters for hydrogen atoms, and bond lengths and angles (7 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the Nitrosyl Ligand/Lewis Acid Adduct $(\eta^5\text{-}C_5H_5)Re(NO \cdot BCl_3)(PPh_3)(SiMe_2Cl)$

Lewis acids form a rich array of adducts with carbonyl ligands of transition-metal complexes.[1] Some are isolable, whereas others can only be detected spectroscopically. Such interactions catalyze or promote a variety of transformations.[1] However, less is known about nitrosyl ligand/Lewis acid adducts.[2–4] Some have been characterized in solution by IR spectroscopy,[3] and Legzdins has recently isolated $AlMe_3$ and MgI_2 complexes of $(\eta^5\text{-}C_5H_5)W(R)_2(NO)$ in analytically pure form.[4] Nitrosyl ligand/Lewis acid interactions have also been shown to play a key role in the catalytic oxidation of alcohols by a cobalt nitro/nitrosyl couple.[5] However, structurally characterized adducts have not to our knowledge been described. In this communication, we report the synthesis, crystal structure, and reactions of the nitrosyl ligand/BCl_3 adduct $(\eta^5\text{-}C_5H_5)Re(NO \cdot BCl_3)(PPh_3)(SiMe_2Cl)$ (**1**).

The previously reported functionalized silyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2H)$ (**2**; ν_{NO} 1636 cm^{-1} (KBr))[6] was dissolved in $CHCl_3$ at 50 °C (Scheme I). Workup gave the chlorosilyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SiMe_2Cl)$ (**3**)[7] as orange needles (84%). Complex **3** exhibited a strong IR ν_{NO} at 1656–1657 cm^{-1} (CH_2Cl_2, KBr)—somewhat low for a linear nitrosyl ligand,[2] but typical for neutral $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds.[8]

In connection with another synthetic objective, a CD_2Cl_2 solution of **3** was treated with BCl_3 (1.1 equiv, 1.0 M in CH_2Cl_2) at −78 °C. NMR spectra (−72 °C) showed downfield shifts of the cyclopentadienyl and methyl ^1H resonances and an upfield shift of the PPh_3 ^{31}P resonance.[9] A ^{11}B NMR spectrum showed a broad peak (7.1 ppm vs $BF_3 \cdot OEt_2$) that was upfield of BCl_3 and in a range characteristic of Lewis base/BCl_3 adducts.[10]

A second equivalent of BCl_3 was added to the **3**/BCl_3 mixture. Extremely air sensitive, orange microcrystals precipitated. In a separate experiment, a CH_2Cl_2 solution of **3** and BCl_3 (2 equiv) was kept at −25 °C. Orange cubes formed (72%).[11] NMR

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