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Synthesis, Crystal Structures, and Thermolysis Studies of Heteronuclear Transition Metal Aluminum Alcoholates

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Abstract. Heteronuclear alcoholate complexes $[M{Al(OiPr)_4}_2(bipy)]$ (**2-M**, M = Fe, Co, Ni, Cu, Zn) and $[M{Al(OcHex)_4}_2(bipy)]$ (**3-M**, M = Fe, Co, Ni, Zn) are formed by adduct formation of $[M{Al(OiPr)_4}_2]$ (**1-M**, M = Fe, Co, Ni, Cu, Zn) with 2,2'-bipyridine and transesterification reaction with *c*HexOAc. According to crystal structure analyses, in **2-M** and **3-M** the central transition metal ion M^{2+} is coordinated by two chelating $Al(OR)_4^-$ moieties and one bipyr-

Introduction

Increasing interest in alcoholate compounds since 1950 lead to the synthesis of alcoholates of nearly every stable metal in the periodic table, and their reactivity was investigated.^[1] These compounds, in principle, can act as single-source precursors (SSPs) to synthesize binary or multinary metal oxides.^[2–5] They can be applied in different synthesis strategies, like sol-gel, hydrothermal, CVD (chemical vapor deposition) or other thermolytic processes.^[6–20] The properties of ternary oxides can be modified in a broader range compared to binary oxides, since a second metal ion establishes another opportunity to modify the structural properties. Therefore, material properties for applications, such as semi-conductivity, magnetism or superconductivity, can be adjusted.^[21–28] For that reason, the interest in synthesis of heteronuclear alcoholates, which contain different types of metal ions, is quite high.

Various heteronuclear aluminum alcoholates were investigated by *Mehrotra* and co-workers in several studies.^[29–48] Starting from water-free metal chlorides, compounds like $[M{Al(OR)_4}_2]$ (M = bivalent transition metal ion, R = *i*Pr, *t*Bu) were synthesized by salt metathesis reaction [Equation (1)]. Derivatives with different organic groups are accessible by alcoholysis reaction with other primary, secondary or terti-

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idine ligand in an octahedral arrangement. Treating **1-Cu** with 2,2'bipyridine leads to a reduction process, whereat the intermediate $[Cu{Al(OiPr)_4}(bipy)_2][Al(OiPr)_4]$ (**4**) could be structurally characterized. During conversion of the *iso*-propanolate ligands in **1-Cu** to cyclohexanolate ligands, Cu²⁺ is reduced to Cu⁺ forming $[Cu{Al(O^cHex)_4}(py)_2]$ (**5**). UV/Vis-spectra and results of thermolysis studies by TG/DTA-MS are reported.

ary alcohols [Equation (2)].^[49] For shifting the equilibrium to the product side, the liberated isopropyl alcohol is distilled off. During that reaction, the steric demand of the alcohol is crucial. If the organic group of the alcohol becomes too demanding, e.g. tBuOH, the alkoxide ligands cannot be substituted quantitatively.^[30] Most of such compounds investigated by Mehrotra and co-workers appear as volatile viscous liquids, except derivatives containing tertiary alkoxides, which form solids. Another possibility to substitute iso-propanolate ligands by other alkoxides is a transesterification reaction [Equation (3)].^[50] The advantage compared to the alcoholysis reaction is the lower coordination ability of esters in contrast to alcohols, so that usually no coordinated solvent molecules are present within the product. Similar to the reaction type in Equation (2), the liberated volatile isopropyl acetate ($T_{\rm b} = 89 \,^{\circ}\text{C}$) can be distilled off to shift the equilibrium to the product side.

$$\mathrm{MCl}_2 + 2 \operatorname{K}[\mathrm{Al}(\mathrm{OR})_4] \rightarrow [\mathrm{M}\{\mathrm{Al}(\mathrm{OR})_4\}_2] + 2 \operatorname{KCl}$$
(1)

(M = divalent transition metal ion, R = iPr, tBu)

 $[M{Al(OiPr)_4}_2] + 8-2x R'OH_{exc.} \rightarrow [M{Al(OR')_{4-x}(OiPr)_x}_2] + 8-2x iPrOH$ (2)

[M = divalent transition metal ion, R' = Me, Et, *n*Bu, *i*Bu, *n*Pr, (x = 0) or *t*Bu, CEtMe₂ (x = 1)]

 $[M{Al(OiPr)_4}_2] + 8 R''OAc_{exc.} \rightarrow [M{Al(OR'')_4}_2] + 8 iPrOAc (3)$

(M = divalent transition metal ion, R'' = nBu, *i*Bu, *n*Pr, *t*Bu, *c*Hex)

Although some of the heteronuclear aluminum alkoxides have been used as SSPs in sol-gel synthesis, systematic thermolysis studies are still rare.^[7–17] Indeed, the thermolysis mechanism of $[Zn{AlH_2(OtBu)_2}_2]$ was clarified during isotope tracing in mass spectrometry experiments and reported by *Veith* and co-workers, but the investigation of the solid residues depending on the included bivalent metal ion is still missing.^[51] This work contributes to that topic as well as to the influence of the 2,2'-bipyridine co-ligand on the thermolysis properties.

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Results and Discussion

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Molecular Structures

The hereronuclear alcoholates 1-M are used as starting materials for compounds 2-M, 3-M, and 5. They are synthesized according to literature procedures, purified by distillation and appear as viscous liquids.^[31,43,47] As shown in Scheme 1, compounds 2-M could be crystallized after adding one equivalent of 2,2'-bipyridine as co-ligand. Since the molecular structures of 2-M show no major differences depending on the divalent cation, compound 2-Co (Figure 1, left) represents a typical example of 2-M. Both aluminum atoms are surrounded by four *iso*-propanolate ligands forming a typical anionic [Al(OiPr)₄]⁻ moiety. Two of these units coordinate to the central divalent cation via two µ2-bridging alcoholate ligands each. The Al-O bonds to terminal iso-propanolate ligands [Al1-O3 169.9(4) pm; Al1–O4 170.0(4) pm] are shorter than to the bridging ones [Al1-O1 177.3(3) pm; Al1-O2 178.1(2) pm] leading to a distorted tetrahedral oxygen environment for the Al³⁺ ions. The coordination sphere of the divalent cation is completed by one 2,2'-bipyridine molecule, which coordinates as chelating ligand, forming a slightly distorted octahedron. The distances of Co²⁺ to the donor atoms vary from 207.8(2) pm (Co1-O2) to 214.8(3) pm (Co1-N1) and the angles from 72.96(9) to 102.51(10)° and 168.47(8) to 170.66(9)°. Typical bond lengths and angles are shown in Table 1.



Scheme 1. Preparation of alcoholates 1-M, 2-M, 3-M, 4, and 5 (M = Fe, Co, Ni, Cu, Zn).

All compounds **2-M** crystallize in the monoclinic crystal system, except triclinic **2-Cu** (see structure data in the Supporting Information). Within the group of monoclinic structures **2-Fe**, **2-Co** and **2-Ni** are isomorphous with space group *C2/c*. Four symmetry equivalent, C₂-symmetric molecules with different orientations of the molecules are present in the unit cell. **2-Zn** crystallizes in the non-centrosymmetric space group *C2* with a smaller angle β and also four different orientations of the molecules in the triclinic space group *P* $\overline{1}$ with four slightly different molecules in the asymmetric unit and eight molecules per unit cell. The independent molecules differ in the length of the two longest Cu–O bonds due to the Jahn–Teller effect of Cu²⁺ ions. The coordination mode



Figure 1. Molecular structures of **2-Co** (top) and **3-Ni** (bottom) as examples for compounds **2-M** and **3-M**. Hydrogen atoms, disordered atoms, and solvent molecules are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (') 1-x, y, 0.5–z.

can be described as a square planar environment (created by two N and two O atoms with similar distances to Cu^{2+}) and two longer Cu–O bonds. The second longest distances vary between 241.7(3) pm (Cu2–O9) and 247.6(3) pm (Cu3–O22), the longest distances vary from 258.2(3) pm (Cu3–O18) to 264.5(3) pm (Cu4–O30).

All compounds **2-M** could be isolated as pure phases as confirmed by PXRD measurements, except **2-Zn**. The latter compound appears polymorphous with structures in space groups C2, Cc and C2/c (unit cell data obtained from Rietveld analyses are reported in Table S1 and Figure S1, Supporting Information). Corresponding packing diagrams of all observed structures are presented in Figure 2. The structures with space group C2 and C2/c show a similar packing which deviates from that in Cc. However, elemental analysis and NMR spectroscopy indicate the isolation of pure **2-Zn**.

During synthesis of **2-Cu**, the blue color changed to brownish-yellow while 2,2'-bipyridine was added. **2-Cu** as well as **4** could be crystallized from this solution. **4** is an ionic comJournal of Inorganic and General Chemistry

01-Al1-O2

01-Al1-O3

89.7(1)

113.8(2)

292.1(1)

208.0(2)

208.9(2)

177.4(2)

172.3(2)

167.57(8)

169.81(8)

168.52(8) 88.79(9)

109.3(1)

06-Ni1-N1

01-Al1-O2

01-Al1-04

Zeitschrift für anorganische alloemeine Chemie Table 1. Selected distances /pm and angles /° in 2-Co, for comparison in 2-Cu, where a Jahn-Teller distortion is observed, and in 3-Ni. 2-Co 2-Cu 3-Ni Ni1…Al1 Co1…Al1 294.4(1) Cu1…Al1 304.7(1)Co1-O1 213.9(2) Cu1-01 200.0(2) Ni1-01 Ni1-N1 Cu1-02 Co1-N1 214.8(3) 243.6(3)Al1-01 177.4(3)Cu1-05 196.2(2)Al1-01 Al1-03 169.9(4) Cu1-06 263.8(3) Al1-04 01-Co1-O1 168.47(8) Cu1-N1 202.8(3)01-Ni1-O5 O2-Co1-N13 170.66(9) Cu1-N2 200.9(3) O2-Ni1-N2

O1-Cu1-N1

O2-Cu1-O6

O5-Cu1-N2



165.7(1)

168.7(1)

165.6(1)

Figure 2. Comparison of packing diagrams of the different structures observed in the powder diffraction pattern of 2-Zn. For clarity, just the metal-donor-atom skeleton is shown.

pound consisting of a cationic $[Cu{Al(OiPr)_4}(bipy)_2]^+$ unit and an [Al(OiPr)₄]⁻ anion (Figure 3). Compound 4 crystallizes in the tetragonal space group $P4_122$ with four molecules per unit cell. Each of the two aluminum atoms in the asymmetric units are surrounded by four alcoholate ligands resulting in a distorted tetrahedral environment. One of them is connected by two μ_2 -bridging alcoholate oxygen atoms to the Cu²⁺ ion whose octahedral coordination is completed by two chelating 2,2'-bipyridine molecules. The organic ligands tend to appear highly disordered (except the μ_2 -bridging ones). Therefore, metal-donor atom distances cannot be discussed accurately. The coordination of the Cu2+ ion can be described as compressed octahedron, which is quiet unusual in terms of Jahn-Teller distortion. However, we cannot exclude that this is the result of a superposition of axially elongated octahedra in the crystal structure caused by disorder. After storage of the mother liquor for three weeks, yellow crystals can be observed which belong neither to 2-Cu nor to 4. Due to the color which is typical for Cu⁺ ions coordinated by pyridine derivatives and due to its high air sensitivity, we assume that a reduction of Cu²⁺ to Cu⁺ occurred. However, the structure could not be clarified so far. Thus, 4 seems to be an intermediate appearing during the reduction of Cu²⁺ to Cu⁺ induced by 2,2'-bipyridine.

For the synthesis of 3-M the iso-propanolate ligands in 1-M are converted to cyclohexanolate ligands by a transesterification reaction with cyclohexylacetate. At 130 °C the formed isopropylacetate is distilled off whereby the equilibrium is shifted towards the product side. Adding 2,2'-bipyridine leads to crystallization of 3-M. All compounds 3-M are isomorphous



Figure 3. Molecular structure (top) and packing diagram (bottom) of the ionic compound 4; hydrogen atoms and disordered atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

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and crystallize in the monoclinic system with space group $P2_1/n$ and four molecules per unit cell. The molecular structure of 3-Ni as a representative compound for 3-M (Figure 1, right) shows the same connectivity between metal ions and ligands as 2-M (typical bond lengths and angles are given in Table 1). Four complex molecules as well as four non-coordinating Et₂O molecules are present in the unit cell. Evacuation of the crystals during the isolation process leads to the loss of solvent molecules, which causes a different XRD powder pattern than expected from single crystal data. The Et₂O molecules can also be extracted from the crystal structure by treating 3-Co with *n*-pentane whereby the crystal structure changes to the triclinic modification with space group $P\bar{1}$. In this single-crystal-to-single-crystal transformation the packing of four molecules in the unit cell remains roughly the same; the unit cell angles change by up to 6° compared to monoclinic **3-Co** (Figure 4 and structure data in Table S3, Supporting Information).



Figure 4. Distortion of the unit cell of **3-Co** due to the loss of solvent molecules.

Using 1-Cu in the procedure for the synthesis of 3-M, reduction of Cu²⁺ to Cu⁺ takes place during heating in cyclohexylacetate, which is indicated by a fading color of the solution. The resulting colorless precipitate could be dissolved in THF, addition of pyridine leads to crystallization of 5 as pale yellow needles. The molecular structure (Figure 5) is similar to that of the compounds $[Cu{Al(OR)_4}(py)_2]$ (R = *i*Pr, *t*Bu) published by Veith and co-workers.^[52] The asymmetric unit consists of three independent molecules, one of which is shown in Figure 5. Compound 5 crystallizes in the monoclinic space group $P2_1/c$. All Al–O bonds range from 171.4(4) pm to 176.0(3) pm to form an AlO₄ tetrahedron. This fragment is connected to the Cu⁺ ion by two µ₂-bridging cyclohexanolate ligands, which show long Cu-O bond lengths. The variation of this Cu-O bond length is the only significant difference between the three molecules within the asymmetric unit. They vary from 220.6(2) pm to 250.5(3) pm. Each [2+2] coordination of the Cu⁺ ions is completed by two pyridine molecules with very similar Cu-N bond length of around 194 pm and N-Cu-N angles between 144.7(1)° and 147.5(1)° (for selected bond lengths and angles see Table 2). The unit cell (Figure 5) contains twelve molecules.



Figure 5. Molecular structure (top) and packing diagram (bottom) of **5**; hydrogen atoms and disordered atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected distances /pm and angles /° in 5.

| 5 | | | |
|---------|----------|-----------|----------|
| Cu1…Al1 | 308.5(1) | N1-Cu1-N2 | 147.2(1) |
| Cu1–O1 | 233.5(3) | N1-Cu1-O1 | 105.6(1) |
| Cu1–O2 | 227.4(3) | O1-A11-O2 | 94.8(1) |
| Cu1–N1 | 194.3(3) | O1-A11-O3 | 112.8(2) |
| Cu1–N2 | 193.9(3) | | |
| Al1-O1 | 174.9(3) | | |
| Al1-03 | 171.3(4) | | |

Thermal Analyses

In order to study compounds **2-M** and **3-M** as precursors for ternary oxides, their thermolytic properties were investigated using TG/DTA-MS measurements. The collected data are summarized in Table 3, typical TG/DTA-MS results are visualized in Figure 6. The observed mass loss of compounds **1-M** and **2-M** is higher than the expected values, because even at ambient pressure these compounds are volatile. In Figure 7 the deviations of the observed mass loss compared to the expected values are shown. Fe²⁺ containing compounds show the highest volatility rates. Due to the co-ligand 2,2'-bipyridine compounds **2-M** are less volatile. In case of **3-M** with the bigger cyclohexanolate ligands the volatility is suppressed completely. Thermolytic properties of complexes **1-M** were investigated under (a) an inert argon atmosphere and (b) an oxidizJournal of Inorganic and General Chemistry

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| | 1 | | | | | |
|----------|------------|------------------------|-------------------|----------------------------------|-------------------------|---|
| Compound | Atmosphere | T_{onset} /°C | $T_{\rm end}$ /°C | $\Delta m_{\rm calcd} = 10^{-3}$ | $\Delta m_{\rm obs}$ /% | Phases in PXRD |
| 1-Fe | argon | 259 | 323 | 70.2 | 95.7 | FeAl ₂ O ₄ |
| | dry air | 242 | 317 | | 74.3 | Fe ₂ O ₃ , Al ₂ O ₃ , FeAlO ₃ |
| 2-Fe | argon | 273 | 321 | 76.5 | 89.8 | γ -Al ₂ O ₃ , Fe, FeAl ₂ O ₄ |
| 3-Fe | argon | 284 | 492 | 83.6 | 83.8 | FeAl ₂ O ₄ , Fe |
| 1-Co | argon | 227 | 328 | 69.8 | 92.0 | Co, γ -Al ₂ O ₃ |
| | dry air | 257 | 320 | | 85.6 | CoAl ₂ O ₄ |
| 2-Co | dry air | 254 | 429 | 76.2 | 85.8 | CoAl ₂ O ₄ |
| 3-Co | dry air | 262 | 515 | 83.3 | 83.3 | CoAl ₂ O ₄ |
| 1-Ni | argon | 247 | 269 | 69.8 | 82.1 | NiAl ₂ O ₄ , Ni, γ -Al ₂ O ₃ |
| | dry air | 235 | 276 | | 79.9 | NiAl ₂ O ₄ , NiO |
| 2-Ni | dry air | 267 | 565 | 76.2 | 81.5 | γ -Al ₂ O ₃ , NiAl ₂ O ₄ , Ni, NiO |
| 3-Ni | dry air | 262 | 568 | 83.4 | 83.7 | γ-Al ₂ O ₃ , NiO, NiAl ₂ O ₄ |
| 1-Cu | argon | 185 | 257 | 69.2 | 86.8 | CuAl ₂ O ₄ , CuAlO ₂ , CuO, |
| | | | | | | Cu ₂ O |
| | dry air | 153 | 259 | | 72.3 | $CuAl_2O_4$, CuO |
| 2-Cu | dry air | 157 | 367 | 75.7 | 81.7 | CuAl ₂ O ₄ , CuO |
| 5 | argon | 113 | 164 | 82.3 ^{b)} | 80.7 | Cu |
| | Ū. | 230 | 254 | | | |
| 1-Zn | argon | 250 | 294 | 69.0 | 82.4 | $ZnAl_2O_4$ |
| | dry air | 249 | 303 | | 84.9 | $ZnAl_2O_4$ |
| 2-Zn | dry air | 233 | 524 | 75.5 | 80.7 | ZnAl ₂ O ₄ , ZnO |
| 3-Zn | dry air | 304 | 547 | 82.8 | 83.2 | $ZnAl_2O_4$ |

| Table 3. Data from TG/E | DTA experiments and dete | ected phases in X-ray powd | ler diffraction patterns of the residues. |
|-------------------------|--------------------------|----------------------------|---|
| | 1 | 1 2 1 | 1 |

a) Calculated for the formation of MAl₂O₄. b) Calculated for the formation of CuAlO₂.

ing atmosphere of dry air. The comparison of both experiments shows the general trend of higher volatility of **1-M** under argon atmosphere due to the absence of oxidative decomposition. During thermolytic experiments of **2-M** an endothermic DTA peak can be assigned to the melting of the substance (Figure 6 and Figures S3–S21, Supporting Information). These melting temperatures are summarized in Table 4.



Figure 6. Idealized thermolysis equation (top) and TG/DTA-MS data (bottom) of the thermolysis of **2-Co** under dry air. TG – solid black line, DTA – blue dashed line, MS ion current with m/e = 15, 43, and 45 – blue, yellow and magenta lines, respectively.

The solid decomposition residues were analyzed by PXRD. In the residue of **1-Fe** only FeAl_2O_4 is found as crystalline phase after thermolysis in an argon atmosphere. In contrast, thermolysis in air leads to oxidation of Fe^{2+} to Fe^{3+} , the formation of binary oxides, Al_2O_3 and Fe_2O_3 , and FeAlO_3 . In the presence of the bipyridine ligand a partial reduction of Fe^{2+} to



Figure 7. Deviation of the observed values of mass loss during TG measurements compared to the expected values.

 Table 4. Melting temperatures (peak temperature) of 2-M observed during DTA measurements.

| | 2-Fe | 2-Co | 2-Ni | 2-Cu | 2-Zn |
|--------------|------|------|------|------|------|
| DTA peak /°C | 157 | 164 | 173 | 161 | 143 |

Fe^{± 0} can be observed under oxygen-free conditions. During thermolysis studies of all cobalt compounds in dry air, phase pure CoAl₂O₄ is formed as a residue, but the reduction of Co²⁺ to Co^{± 0} can be observed when **1-Co** is heated under inert atmosphere. To understand the reduction process, **2-Fe** and **1-Co** were decomposed in larger scale in a nitrogen atmosphere and the formed thermolysis gases were trapped in an NMR tube. In the NMR spectra propene, *iso*-propanol and, in adneine Chemi

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Figure 8. Temperature dependent X-ray powder diffraction pattern (Guinier-Simon diagram, HT-PXRD) of 2-Zn.

dition, acetone could be detected. These products indicate that the *iso*-propanolate ligands act as reducing agents. Presence of the bipy co-ligand favors the reduction of Fe^{2+} to $Fe^{\pm 0}$ so that a partial reduction takes place.

In thermolysis experiments of 1-Ni and 2-Ni, NiAl₂O₄, γ -Al₂O₃, and Ni-containing compounds as by-products are formed. In inert or oxidizing atmosphere nickel metal or NiO, respectively, show up in the diffraction patterns. In addition, $Ni^{\pm 0}$ can be observed in the residue of **2-Ni**, which emphasizes the role of the bipyridine ligand in the reduction process even in dry air. With copper compounds (1-Cu, 2-Cu, and 3-Cu) similar results can be observed. The residue after thermolysis of 1-Cu under argon consists of binary (CuO, Cu₂O) and ternary oxides (CuAl₂O₄, CuAlO₂) with Cu^{2+} and Cu^{+} ions. In contrast, under oxidizing conditions just CuAl₂O₄ and CuO can be detected in XRD powder patterns, also formed Al₂O₃ remains amorphous. Independent of the gas atmosphere, thermolysis of 1-Zn leads to ZnAl₂O₄. The same result is observed for 3-Zn, whereas the thermolysis residue of 2-Zn contains a very small amount of ZnO (< 1 wght-%) which may be caused by a byproduct in the synthesis of 2-Zn.

The thermolysis of the Cu⁺ compound **5** in argon proceeds in two steps of mass loss. The first step ($T_{\text{onset}} = 113 \text{ °C}$, $\Delta m = -25.6 \%$) indicates the loss of pyridine molecules, afterwards, at $T_{\text{onset}} = 230 \text{ °C}$ ($\Delta m = -55.1 \%$) the cyclohexanolate ligands decompose. The residue contains copper metal and amorphous Al₂O₃, the alcoholate ligands may act as reducing agent.

HT-PXRD

The thermal behavior of complexes 2-M was also investigated by temperature dependent PXRD measurements (HT- PXRD). During the heating process, 2-Zn shows a phase transition between 65 and 75 °C forming $[Zn{Al(OiPr)_4}_2(bipy)]$ in space group C2/c (Figure 8, diffraction pattern B), which was identified by comparison with the PXRD pattern of 2-Ni. At 115 °C 2-Zn melts (diffraction pattern C) and re-crystallizes again after cooling down to 50 °C in space group C2/c (diffraction pattern D). This indicates that the thermodynamically favored structure is in the centrosymmetric space group. The varying intensities in diffraction pattern D are caused by texture effects due to a preferred orientation within the sample containing capillary. In another experiment it is proven by Rietveld analysis, that 2-Zn crystallizes in the C2/c structure from its melt (Figure S2, Supporting Information). For 2-Fe, 2-Co and 2-Ni, also melting can be observed, however, without additional phase transitions. In contrast, 2-Cu does not recrystallize after cooling below the melting temperature, but a change in color from blue (2-Cu) to brownish-yellow can be noticed, indicating that a reduction process takes place.

UV/Vis Spectroscopy

Electronic spectra of compounds 1-M, 2-M, 3-M and 5 (M = Fe, Co, Ni, Cu; solution in MTBE) are shown in Figure 9. The d-d transition bands at 297 nm, 1015 nm, and 1312 nm for 1-Fe are characteristic for octahedral Fe²⁺ environment, establishing that the $[Al(OiPr)_4]^-$ fragment acts in solution as tridentate ligand.^[53] The spectra of 2-Fe and 3-Fe show additional charge-transfer bands at 561 nm and 571 nm, respectively.^[54] 1-Co also shows characteristic d-d transitions for octahedral Co²⁺ ions at 499 nm and 551 nm. In addition, a shoulder at 642 nm can be observed, which indicates Co²⁺ in

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Figure 9. UV/Vis spectra of compounds 1-M, 2-M, 3-M, and 5 measured in MTBE as solvent: (a) M = Fe, (b) M = Co, (c) M = Ni, (d) M = Cu.

tetrahedral environment.^[43] Here, the $[Al(OiPr)_4]^-$ group acts as tridentate and bidentate ligand. This behavior can also be observed for **1-Ni**, where the d–d bands for tetrahedrally surrounded Ni²⁺ ions (527 nm and 578 nm) are clearly visible as well as the absorptions for octahedral Ni²⁺ environment (426 nm and 784 nm).^[44,55] The complexes **2-Co**, **2-Ni**, **3-Co** and **3-Ni** exhibit just characteristic d–d bands for sixfold coordinated M²⁺ ions. The copper compounds **1-Cu** and **2-Cu** display similar spectra with a broad band at 699 nm and 718 nm, respectively. These belong to d–d transitions of octahedral Cu²⁺ ions with Jahn–Teller distortion.^[33,42,46] In the UV/Vis spectrum of Cu⁺ containing compound **5** just π – π * transitions of pyridine molecules are observed as well as a charge-transfer band at 335 nm.^[56]

Conclusions

The new heteronuclear alcoholate complexes $[M{Al(OiPr)_4}_2(bipy)]$ (2-M, M = Fe, Co, Ni, Cu, Zn) and $[M{Al(OcHex)_4}_2(bipy)]$ (3-M, M = Fe, Co, Ni, Zn) were successfully synthesized from $[M{Al(OiPr)_4}_2]$ (1-M) and 2,2'-bipyridine, and in case of 3-M, by a transesterification reaction prior to the adduct formation. The crystal structures of 2-M and 3-M were determined. During synthesis of 2-Cu a bipy ligand induced reduction process occurred, where the structure of intermediate $[Cu{Al(OiPr)_4}(bipy)_2][Al(OiPr)_4]$ (4) could

be identified. In addition, a thermally induced reduction of 1-Cu can be observed during transesterification reaction leading to the Cu⁺ compound $[Cu{Al(OcHex)_4}(py)_2]$ (5). In thermolvsis studies under argon atmosphere a reduction of M^{2+} to $M^{\pm 0}$ takes place depending on the type of M²⁺ cation. Fe/Fe²⁺ represents a limiting redox pair for the reduction process, whereat in presence of 2,2'-bipyridine reduction occurs more easily. The alcoholate ligands act as reducing agents, as evident by the detection of acetone as a volatile thermolysis product. Depending on the gas atmosphere, phase pure $FeAl_2O_4$, $CoAl_2O_4$, and ZnAl₂O₄ could be synthesized under mild conditions, as confirmed by powder X-ray diffraction. Thus, the required reaction temperatures are significantly lower than typical solidstate reactions. 2-M and 3-M might be useful in processes like CVD, sol-gel synthesis or liquid phase assisted techniques due to their high solubility in organic solvents.

Experimental Section

Materials and General Procedures: All manipulations were carried out in a nitrogen atmosphere using standard Schlenk technique or an MBRAUN UniLab glovebox. Solvents were dried with sodium or CaH₂ and distilled prior to use. Potassium, NiCl₂ and 2,2'-bipyridine were purchased from Acros Organics, ABCR and TCI, respectively, and used without further purification. Cyclohexylacetate (TCI) was distilled from CaH₂, and Al(O*i*Pr)₃ (Sigma Alrich) was recrystallized from *n*-pentane. Unhydrous CuCl₂ was obtained by heating Zeitschrift für anorganische und allgemeine Chemie

CuCl₂·2H₂O in vacuo. CoCl₂ and ZnCl₂ were generated by drying CoCl₂·6H₂O and ZnCl₂·4H₂O with SOCl₂.^[57] Water-free FeCl₂ was prepared by dissolving iron in methanol by addition of concentrated hydrochloric acid. The obtained FeCl₂·*x*MeOH was decomposed in vacuo at 180 °C to form FeCl₂.^[58]

Synthesis of $[M{Al(OiPr)_4}_2]$ (1-M, M = Fe, Co, Ni, Cu, Zn): This reaction was performed according to literature procedures.^[31,43,47] In a typical synthesis 1.57 g (40 mmol, 2 equiv.) of potassium metal was dissolved in 20 mL isopropyl alcohol and then added to a suspension of 8.19 g (40 mmol, 2 equiv.) $Al(OiPr)_3$ in 35 mL *i*PrOH and stirred overnight. The resulting solution was mixed with a stirred suspension of 1 equiv. of the anhydrous metal chloride in 15 mL *i*PrOH and refluxed for 24 h. The precipitated KCl was separated and the solvent removed under reduced pressure. The crude product was purified by distillation in vacuo. In case of 1-Ni the crude product was dissolved in toluene. The solvent was distilled off prior to vacuum distillation to remove coordinated *i*PrOH molecules. 1-M appears as a viscous liquid in 38–67% yield. Experimental details are given in the Supporting Information.

Synthesis of $[M{Al(OiPr)_4}_2(bipy)]$ (2-M, M = Fe, Co, Ni, Cu, Zn): In a typical synthesis, 156 mg (1 mmol, 1 equiv.) of 2,2'-bipyridine was added to a solution of an equimolar amount of 1-M (1 mmol, 1 equiv.) in *n*-pentane. The mixture was kept stirring for 1 h at room temperature. Crystals of 2-M could be isolated after cooling the solution to -25 °C with 25-70% yield. After several days, crystals of 4 could be observed from the copper containing reaction mixture. Further details are given in the Supporting Information.

Synthesis of $[M{Al(OcHex)_4}_2(bipy)]$ (3-M, M = Fe, Co, Ni, Zn): A solution of 2 mmol (1 equiv.) 1-M in 10 mL cyclohexylacetate was heated to 130 °C for 4–6 h. After removing the solvent, the residue was dissolved in a *n*-pentane/Et₂O mixture (1:2 V/V), and 312 mg (2 mmol, 1 equiv.) 2,2'-bipyridine was added. Crystals of 3-M·Et₂O can be isolated by cooling the mother liquor to –25 °C with 48–67% yield. Details are given in the Supporting Information.

Synthesis of $[Cu{Al(OcHex)_4}(py)_2]$ (5): A solution of 0.75 g (1.3 mmol, 1 equiv.) **1-Cu** in 11 mL cyclohexylacetate was heated to 140 °C for 3 h. After cooling the reaction mixture to room temperature, the colorless precipitate was separated and dispersed in 10 mL THF. Addition of 0.5 mL pyridine lead to crystallization of **5** (yield: 239 mg (56%)) by cooling the mother liquor to 2 °C. Details are given in the Supporting Information.

Characterization: TG-DTA analysis was performed in an argon or dry-air atmosphere with a Netzsch STA 449 F1 thermobalance (heating rate 10 K·min⁻¹) connected to an Aeolos QMS 403 D mass spectrometer. Elemental analyses were measured with a Vario El by Heraeus, UV/Vis spectra with a V-670 spectrometer by Jasco. NMR spectra were measured with a Bruker DPX-400 (¹H: 400 MHz, ¹³C: 100 MHz), the signals were referenced to solvent signals.

Crystal Structure Analyses: Single crystal diffraction data were collected on an imaging plate diffractometer system STOE IPDS-2T equipped with a sealed Mo X-ray tube and a graphite monochromator crystal [λ (Mo- K_{α}) = 71.073 pm] or on a STOE Stadivari system with a Cu microfocus X-ray source [λ (Cu- K_{α}) = 154.186 pm], a multi-layer mirror and a Dectris Pilatus-300K detector. Data processing was carried out with STOE X-Area software including a numerical absorption correction and scaling routine.^[59] The structures were solved by direct methods using SHELXT and refined by using SHELXL-2014.^[60] All non-hydrogen and non-disordered atoms were refined with anisotropic

thermal parameters. Hydrogen atoms were included on idealized positions. The structures were visualized using Diamond 3.2k.^{(61]} The crystallographic data are summarized in the Supporting Information (Tables S2–S4, Supporting Information).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2007715, CCDC-2007716, CCDC-2007717, CCDC-2007718, CCDC-2007719 for **2-M**, CCDC-2007720, CCDC-2007721, CCDC-2007722, CCDC-2007723, CCDC-2007724 for **3-M**, CCDC-2007962 for **4**, and CCDC-2007725 for **5** (Fax: +44-1223-336-033; E-Mail: structures@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk).

Powder X-ray Diffraction: Powder XRD patterns were measured with a STOE STADI-P diffractometer system equipped with a sealed Cu X-ray tube, a germanium (111) monochromator crystal [λ (Cu- K_{a1}) = 154.060 pm] and a Dectris Mythen-1 K detector. The alcoholate complexes were measured in Debye–Scherrer setup in glass capillaries (Hilgenberg, 0.5 mm), thermolysis products were measured as flat samples on polymer films in transmission mode at room temperature. For temperature dependent measurements sample-filled capillaries were rotated in a high temperature device (Type 2416 by EURO-THERM). Data processing was carried out with STOE WinXPOW.^[62] Rietveld analysis was performed with Bruker TOPAS 5 using the fundamental parameter approach.^[63] The crystallographic data as references for qualitative and quantitative analysis of the powder diffraction patterns are taken from the literature.^[64–77]

Supporting Information (see footnote on the first page of this article): Experimental details, crystallographic data, TG/DTA-MS data and Rietveld analyses of the solid residues, HT-PXRD measurements of **2-M**, UV/vis spectrum of **5**, NMR spectra of **1-Zn**, **2-Zn**, **3-Zn** and of trapped volatile thermolysis products are provided as supporting information.

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