Synthesis and Structure of Novel Complexes of Gallium

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Dedicated to Prof. G. Schmid on the occasion of his 60th birthday

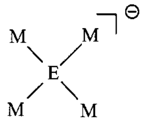
Keywords: Metathesis / Iron / Gallium / Cobalt / Cyclopentadienyl ligands

$[Cp^{*}GaCl_2]$ ($Cp^{*} = \eta^1\text{-}C_5Me_5$) reacts with $K[Co(CO)_4]$ with elimination of KCp^{*} and KCl to form the novel ionic complexes $[K(toluene)_2][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ (**1**) and $K[GaCl\{Co_2(CO)_6(\mu\text{-}CO)\}\{Co(CO)_4\}]$ (**2**), where the gallium atoms possess the coordination number four. The reaction of $[\{Co(CO)_4\}_2GaCl(THF)]$ with $LiCp^{*}$ leads to the ionic product $[Li(THF)][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ (**3**). The $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ anions of **1** and **3** represent the first homoleptic spirocyclic coordination mode of gallium. The reaction of $GaCl_3$ with $Na_2[Fe(CO)_4]$ leads to the ionic compound $[Na(OEt_2)_2][Fe(CO)_4(GaCl_3)_2]$ (**4**). Complexes **1**, **2**, **3** and **4** were characterised by X-ray structure analysis and IR spectroscopy. Additionally, ESI mass spectra of **1** were recorded at different cone voltages, where the molecular ion peak of the anion $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ as well as the peaks resulting from sequential loss of CO ligands until the formation of the naked $[Co_4Ga]^-$ cluster are observed. The ionic complexes **1**, **2**, **3** and **4** form polymeric networks through coordination of their cations. In **2** a three-dimensional polymeric network is formed by coordination of the Co_3Ga units and their K counterions, whereas in **1** the K ions are additionally coordinated by toluene molecules to form dimeric macrocyclic motifs by coordination of two of the anionic Co_4Ga units. In **3** a zigzag chain is formed by coordination of the Co_4Ga units through their Li cations. In the crystal packing of complex **4** the $FeGa_2$ moieties form zigzag chains, coordinating through their Na counterions.

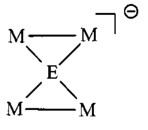
Introduction

Metathesis reactions of group 13 element halides with carbonyl metalates represent a useful method to synthesise compounds with covalent transition metal-main group bonds. The majority of complexes thereby obtained possesses coordination numbers (CN) of three and four with exclusively trigonal planar and tetrahedral coordination modes, respectively. Depending on the reaction conditions competing reactions occur, for example the formation of anionic complexes of CN 4.[1] Among complexes of CN 4 of the general type $E(ML_n)_4^-$ (E = Al, Ga, In, Tl; ML_n = transition metal fragment), which can alternatively be regarded as Lewis base adducts of the type $E(ML_n)_3$, the coordination modes **A**, **B** and **C** are possible.

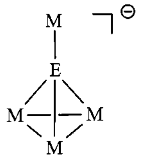
For complexes of type **A**, examples exist for E = In and Tl, such as $[In\{Co(CO)_4\}_4]^-$,[2] whereas for **B** the indium complexes $[In\{Fe_2(CO)_8\}_2]^-$,[3] $[\{(\mu\text{-}H)Mn_3(CO)_{12}\}_2(\mu_4\text{-}In)]$[4] and $[\{Re(CO)_3(\mu\text{-}I)_2Re(CO)_3\}In\{Re(CO)_4(\mu\text{-}I)Re(CO)_4\}]$[5] are the only known representatives. For gallium only $[Re_3(CO)_9(Ph_3P)_3(\mu\text{-}Cl)_3(\mu_3\text{-}\{GaRe(CO)_4(Ph_3P)\})]$ and the Re_4Ga_4 cluster $[Re_4(CO)_{12}\{\mu_3\text{-}\{GaRe(CO)_5\}_4]$[6] are known for type **C**; examples of the coordination modes **A** and **B** are as yet unknown for gallium. We report herein on the synthesis of the first examples for gallium with the coordination mode **B**.



A



B



C

Results and Discussion

The reaction of Cp^*GaCl_2 ($Cp^* = \eta^1\text{-}C_5Me_5$) with $K[Co(CO)_4]$ in Et_2O or THF results in the formation of the ionic heteronuclear clusters $[K(toluene)_2][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ (**1**) and $K[GaCl\{Co_2(CO)_6\}(\mu\text{-}CO)\}\{Co(CO)_4\}]$ (**2**), respectively, in high yields [Equation (1) and (2)]. Although the workup of **2** was carried out by extraction with toluene, as was the case for **1**, no solvated toluene was found in the crystal lattice of **2**. The results show that besides the KCl elimination, Cp* removal also occurs as a competing reac-

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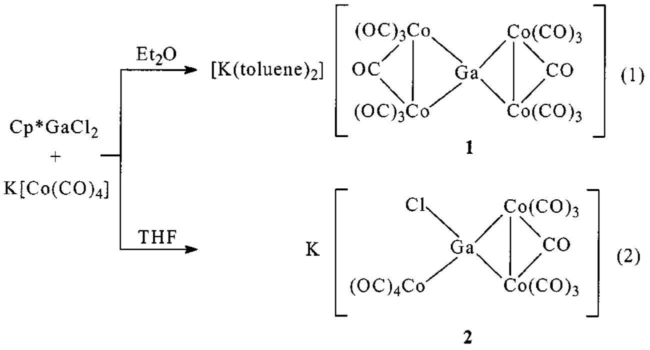
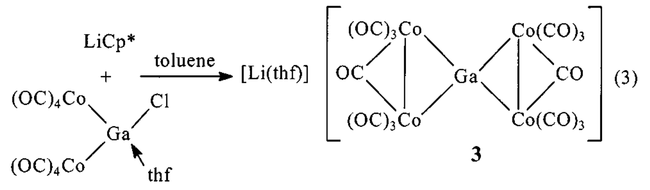
tion. Furthermore, the reaction in donor solvents seems to favour the formation of ionic complexes. Complex **2** can be regarded as a formal precursor molecule of **1**, from which Cl substitution by $Co(CO)_4^-$ leads to the formation of the spirocyclic complex **2**.



Surprisingly, we found that the reaction of $[\{Co(CO)_4\}_2GaCl(THF)]$ with LiCp* in toluene at −78 °C leads to the ionic product $[Li(THF)][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ **3** [Equation (3)].



Complexes **1** and **3** represent the first examples of the coordination mode **B** where the Ga atom is additionally homoleptically coordinated by metal atoms.

Complexes **1** and **3** are orange and **2** red-brown crystalline compounds, which are readily soluble in toluene, THF and CH_2Cl_2. In their IR spectra, CO stretching frequencies for terminal and bridging CO ligands are observed.

The ionic complex **1** crystallises in the triclinic space group $P\bar{1}$ with two independent molecules (A and B) in the asymmetric unit, which reveal similar structural features.[7] Each of the K counterions possesses two coordinated toluene molecules. Figure 1 shows the molecular structure of the anion $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ of one of the independent molecules (molecule A) of **1**. The gallium atom is bound side-on to two $[\{Co(CO)_3\}_2\{\mu\text{-}CO\}]$ groups to form a spirocyclic compound containing two Co−Ga−Co three membered rings. These rings are bent by 82.55(4)° (molecule A) and 87.58(4)° (molecule B). Alternatively, the structure of **1** can be described as a distorted Co_4 tetrahedron centred by a Ga atom.

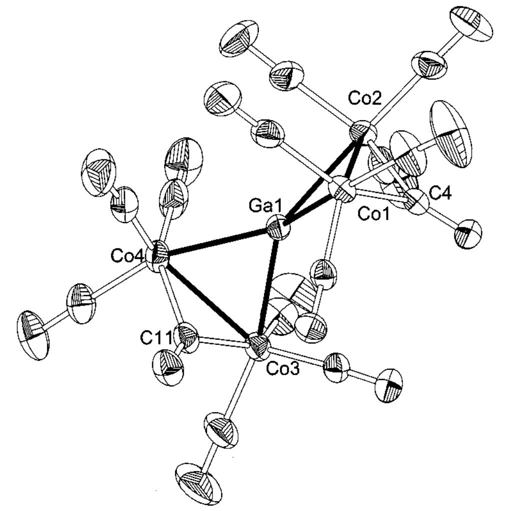


Figure 1. Molecular structure of the $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ anion of one of the independent molecules (molecule A) of **1** in the crystal (showing 30% probability ellipsoids); selected bond lengths [Å] and angles [°]: Ga1−Co1 2.442(1), Ga1−Co2 2.397(1), Ga1−Co3 2.396(1), Ga1−Co4 2.451(1), Co1−Co2 2.588(1), Co3−Co4 2.562(1), Co1−C4 1.907(4), Co2−C4 1.925(4), Co3−C11 1.925(4), Co4−C11 1.904(4); Co1−Ga1−Co2 64.66(3), Co3−Ga1−Co4 63.78(3)

The Co−Co bond lengths in both independent molecules [2.560(1) to 2.588(1) Å] are similar to the Co−Co bond length in $Co_2(CO)_8$ [2.528(1)−2.530(1) Å];[8] the Co−Ga bonds [2.395(1)−2.454(1) Å] are in the range of known Co−Ga bond lengths as in, for example, $[(CO)_3Co\{\mu\text{-}(\eta^5\text{-}Cp^*Ga)\}_2Co(CO)_3]$ [2.3784(5)−2.3959(5) Å].[9] In addition to the molecular structure of anion **1** described above, the location of the K atom and its coordinated toluene molecules are depicted in the crystal lattice in Figure 2. Both independent $GaCo_4$ units of **1** are bridged through their K counterions to form a dimer in which each K atom is coordinated by four CO ligands (a terminal and a bridging CO moiety of each anion of **1**) and two molecules of toluene. The macrocycle thus formed contains eight heavier atoms (gallium, cobalt and potassium), and two such macrocycles form the unit cell. The formation of the macrocyclic dimer of **1** in the crystal leads to the small structural

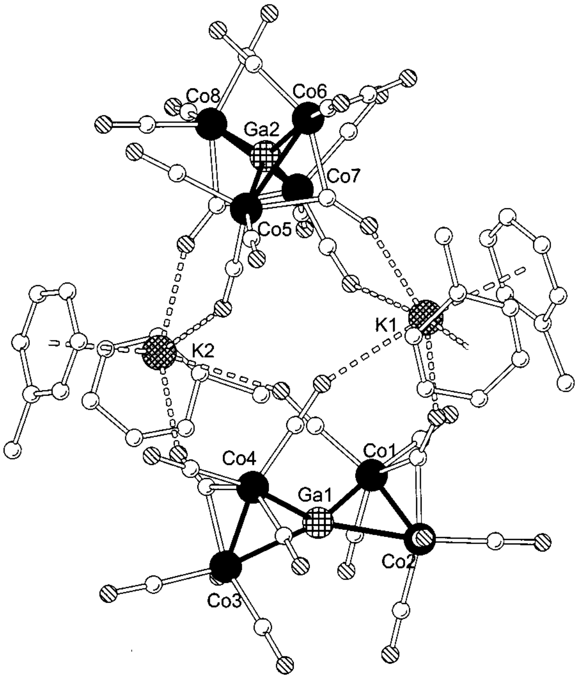


Figure 2. Formation of macrocyclic dimers in the crystal lattice of **1** (H atoms of the toluene molecules are omitted for clarity)

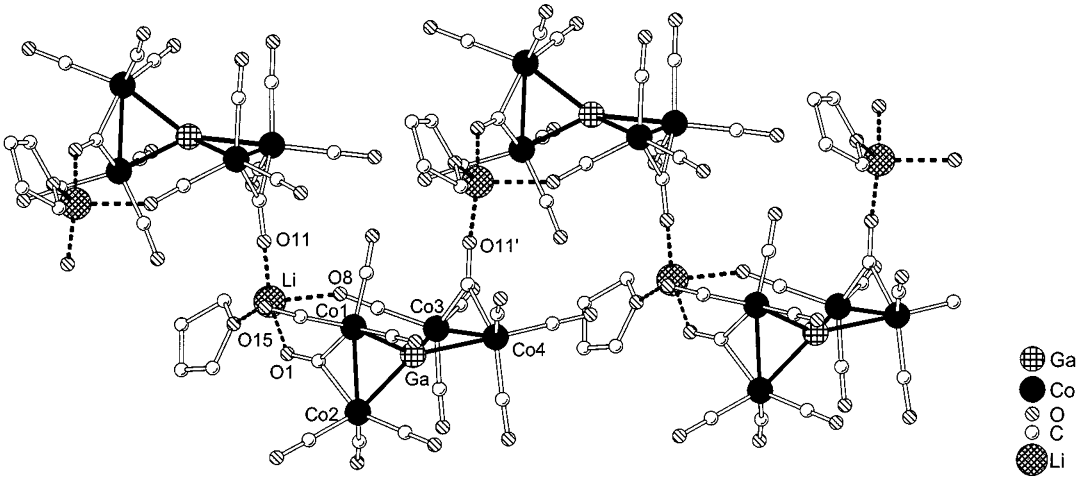


Figure 3. Structure of **3** in the crystal lattice; selected bond lengths [Å] (H atoms of the toluene molecules are omitted for clarity): Ga−Co1 2.439(1), Ga−Co2 2.398(1), Ga−Co3 2.453(1), Ga−Co4 2.398(1), Co1−Co2 2.557(1), Co3−Co4 2.576(1), Li−O1 1.946(13), Li−O8 2.17(2), Li−O11 1.904(13), Li−O15 1.807(13)

differences between the independent molecules of **1**. Thus, the Co−Ga−Co bond angles in molecule B are very similar [63.72(4)° and 63.96°], whereas those in molecule A differ slightly more [64.66(3)° and 63.78(3)°].

Complex **3** crystallises as one enantiomer in the orthorhombic space group $P2_12_12_1$, with four formula units in the asymmetric unit cell. The molecular structure of the anion of **3** is similar to the structure of the anion of **1** (Figure 1), where similar bond lengths and angles are observed. In contrast to **1**, **3** possesses Li counterions, which are coordinated by THF molecules. A view of the packing of **3** in the crystal lattice is shown in Figure 3, and is clearly different to that of **1**. Each of the $GaCo_4$ moieties in **3** is connected by two Li cations to the next molecular units establishing an overall zigzag chain forming a chiral helix. The Li counterions are fourfold coordinated by three O atoms of the CO ligands and the O atom of a THF molecule.

The existence of the $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ anions of **1** and **3** in solution was further proved by Electrospray-Ionisation (ESI) mass spectrometry using a high resolution FT-ICR mass spectrometer.[10] Figure 4a shows the observed molecular ion peak of the anion $[Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]^-$ of **1** (cone voltage = 20 V), which, as can clearly be seen from Figure 4b, is in good agreement with the simulated mass distribution at m/z = 696 $[^{69}Ga(^{12}CO)_{14}Co_4]$. The mass spectrum of the cation of **1** shows only the peak for the K^+ cation. In further experiments the fragmentation behaviour of the anion of **1** at continuously increasing cone voltages was investigated. A stepwise elimination of CO was found with a steadily increasing voltage, and all the fragments up to the naked $[Co_4Ga]^-$ cluster (cone voltage of 240 V) were detected. This result shows the exceptional stability of the $GaCo_4$ cluster core.

The ionic complex **2** crystallises in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The molecular structure of the $[GaCl\{Co_2(CO)_6\}(\mu\text{-}CO)\}\{Co(CO)_4\}]^-$ anion of **2** is depicted in Figure 5. The gallium atom is in a distorted tetrahedral geometry surrounded by one Cl and three Co atoms. The metal-metal bond between the Co1 and Co2 atoms is bridged by a CO ligand. The Co−Co [2.595(1) Å] and the Co−Ga bond lengths [2.419(1), 2.441(1) and 2.448(1) Å] of **2** are similar to those observed in **1** [2.396(1)−2.451(1) Å]. The angle between the planes formed by the atoms Co1−Ga−Co2 and Cl−Ga−Co3 is 83.96(3)°. In contrast to the macrocyclic

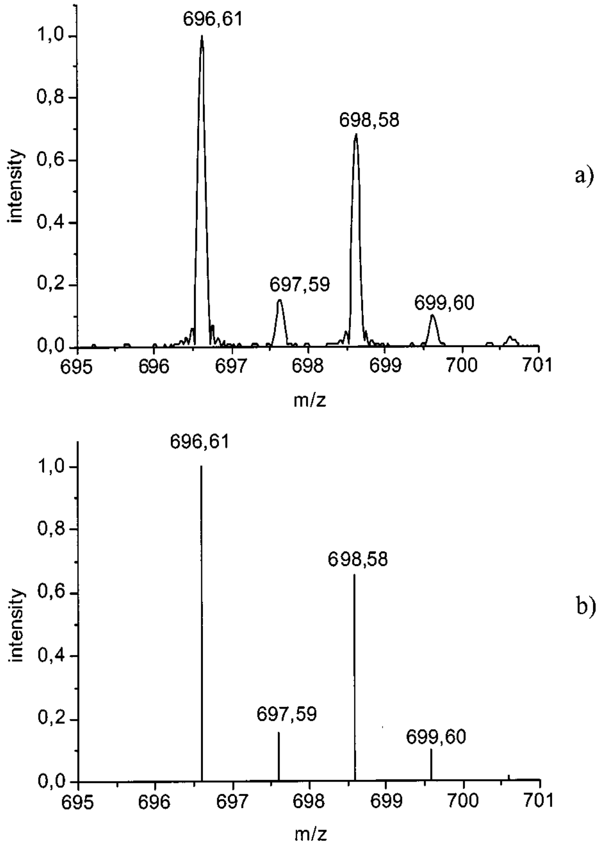


Figure 4. ESI mass spectrum of **1**: a) experimental at a cone voltage of 20 V; b) calculated

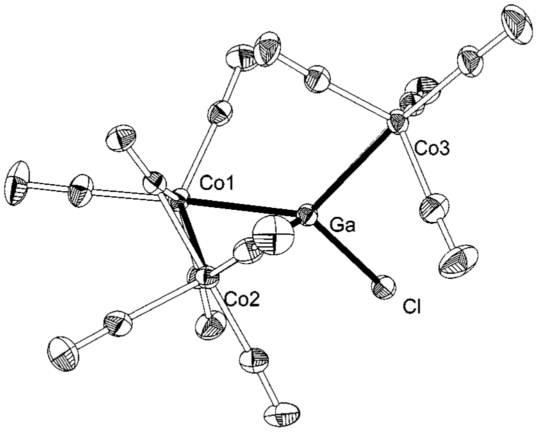
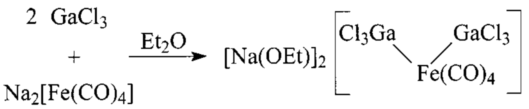


Figure 5. Molecular structure of the $[GaCl\{Co_2(CO)_6\}(\mu\text{-}CO)\}\{Co(CO)_4\}]^-$ anion of **2** in the crystal (showing 30% probability ellipsoids); selected bond lengths [Å] and angles [°]: Ga−Co1 2.441(1), Ga−Co2 2.419(1), Ga−Co3 2.448(1), Co1−Co2 2.595(1), Ga−Cl 2.304(1); Co1−Ga−Co2 64.54(2), Cl−Ga−Co2 118.66(3), Cl−Ga−Co1 112.34(3), Cl−Ga−Co3 102.30(3), Co2−Ga−Co3 125.71(2), Co1−Ga−Co3 131.00(3)

dimeric structure in the crystal lattice of **1** and the zigzag-chain of **3**, the $GaCo_3$ clusters of **2** coordinate to the unsolvated K atoms to form a three-dimensional network. A view of a layer along the crystallographic *c* axis of the crystal packing structure of **2** is depicted in Figure 6. The $GaCo_3$ units of **2** are similarly oriented along the crystallographic *a* axis, whereas they are alternately twisted along the *b* axis. Each of the K atoms is ninefold coordinated by seven O atoms of the CO ligands (terminal as well bridging CO) and by two Cl atoms. The K atoms along the *a* axis are oriented above and below the presented plane, and each are coordinated by five $GaCo_3$ moieties, three of which are shown in Figure 6.

The reaction of $GaCl_3$ with $Na_2[Fe(CO)_4]$ in Et_2O at 0 °C leads to the ionic addition product $[Na(OEt_2)]_2[Fe(CO)_4(GaCl_3)_2]$ **4** [Equation (4)], which was isolated as colourless crystals. Complex **4** is readily soluble in donor solvents like Et_2O and THF. In the IR spectrum of **4**, only bands for terminal CO groups are found.



(4)

4

Complex **4** crystallises in the monoclinic space group $P2_1/c$ with four formulae units in the asymmetric unit cell. The molecular structure of the anion of **4** is depicted in Figure 7. The central Fe atom is octahedrally surrounded by four CO ligands and two *cis*-oriented $GaCl_3$ moieties. The axial carbonyl ligands of the $Fe(CO)_4$ unit are unexpectedly strongly bent towards the $GaCl_3$ groups, probably due to the Lewis acid character of the group 13 atoms. The Ga−Fe bond lengths [2.409(1) and 2.411(1) Å, respectively] are slightly longer than in $[(CO)_4FeGaCl_2(tmeda)]$ [2.338(1) Å].[11]

A view of the packing of **4** in the crystal lattice is shown in Figure 8. Each of the $GaCl_3$ moieties in **4** is connected via two Na cations to the next molecular unit establishing

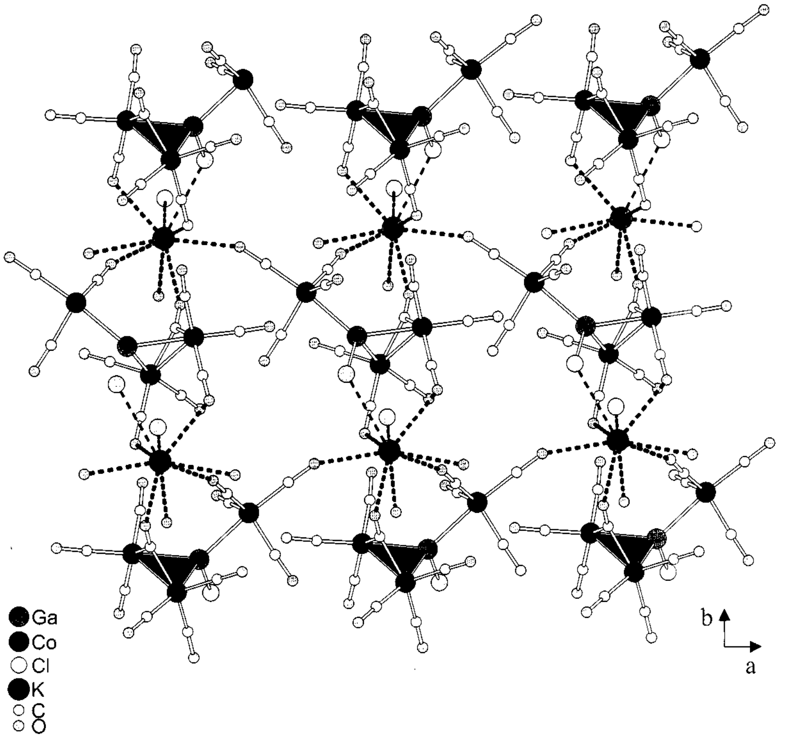


Figure 6. View along the crystallographic *c* axis in the crystal lattice of **2** (the Co_2Ga planes are marked); the coordinating O and Cl atoms of the K atoms above and below the *a,b* plane are depicted without their connecting cluster units for clarity

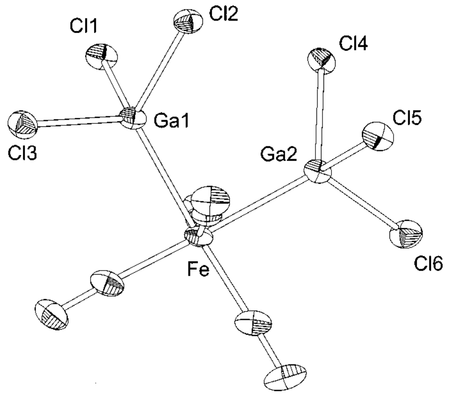


Figure 7. Molecular structure of the $[Fe(CO)_4(GaCl_3)_2]^{2-}$ anion of **4** in the crystal (showing 30% probability ellipsoids); selected bond lengths [Å] and angles [°]: Ga1−Fe 2.409(1), Ga2−Fe 2.411(1); Ga1−Fe−Ga2 90.74(3)

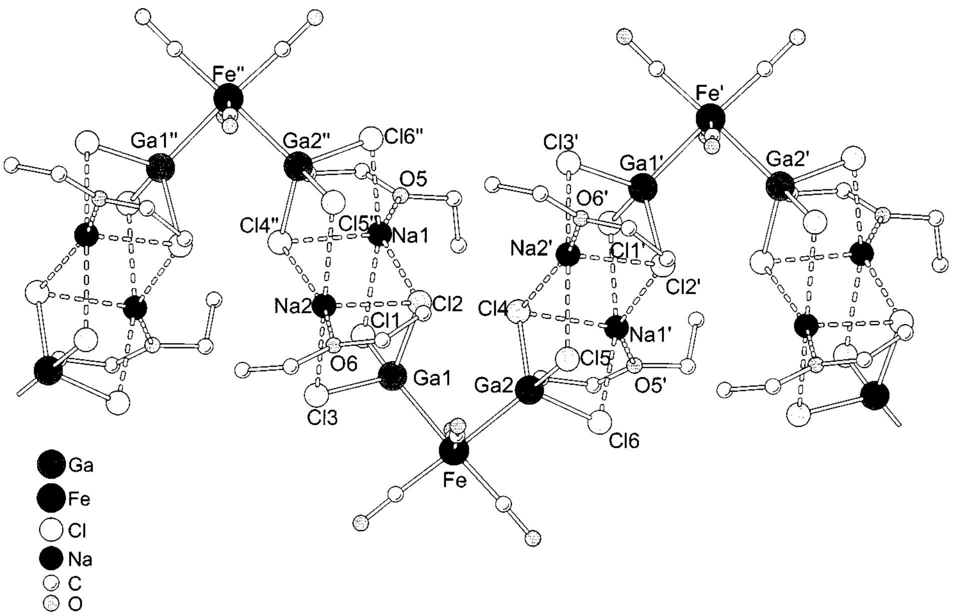


Figure 8. Structure of **4** in the crystal lattice; selected bond lengths [Å] and angles [°] (H atoms of the toluene molecules are omitted for clarity): Na1···Cl1 2.789(2), Na1···Cl2 2.818(2), Na1···Cl4 2.883(2), Na1···Cl6 2.799(2), Na2···Cl2 2.853(2), Na2···Cl3 2.779(2), Na2···Cl4 2.877(2); Cl5···Na2···Cl2 95.19(6), Cl3···Na2···Cl4 95.19(6).

an overall zigzag chain. The Na ions are fivefold coordinated by four Cl atoms and an O atom of the coordinated ether molecule.

Conclusions

We have shown that the reaction of Cp^*GaCl_2 and $GaCl_3$ with transition metal metalates leads to the formation of ionic compounds forming polymeric structures in the crystal lattice. Whereas the solvation of the K counterion in **1** by toluene leads to a macrocyclic dimer, the Li counterion in **3**, due to its lower coordination number, leads to a chiral zigzag chain-like structure. The absence of solvent molecules in **2** leads to the formation of a 3D polymeric network. The degree of aggregation is strongly determined by the coordination of the counterions and the coordinated solvent molecules. Since the workup of **1** and **2** was carried out identically, the coordination of the toluene molecules in **1** seems to be the determining factor for the formation of macrocycle **1**.

Experimental Section

General Techniques: All manipulations were performed under an atmosphere of dry N_2 using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. Gallium trichloride was obtained commercially and used without further purification. The starting materials Cp^*GaCl_2 [12] and the compounds $K[Co(CO)_4]$[13] and $Na_2[Fe(CO)_4]$[14] were prepared according to literature methods. The ESI mass spectra were recorded on a Bruker APEX II Fourier-Transform-ICR mass spectrometer and the IR spectra on a Bruker IFS 28.

$[K(toluene)_2][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ (1): A solution of Cp^*GaCl_2 (0.138 g, 0.5 mmol) in Et_2O (10 mL) was slowly added at −78 °C to a solution of $K[Co(CO)_4]$ (0.231 g, 1.1 mmol) in 10 mL Et_2O. The reaction mixture was stirred for 14 h and was then allowed to warm to room temperature. The resulting yellow solution was filtered through silica and all of the solvent was removed in vacuum. The yellow residue was extracted with 20 mL toluene and the solution was reduced to 2 mL. At −30 °C orange crystals of $[K(toluene)_2][Ga\{Co_2(CO)_6(\mu\text{-}CO)\}_2]$ (**1**) were formed (244 mg, 70%). IR (KBr): $\tilde{\nu}$ = 1968(s) cm^{-1}, 1764(m) ν(CO). MS (ESI): *m/z* = 696 $[M^-]$.

$K[GaCl\{Co_2(CO)_6\}(\mu\text{-}CO)\}\{Co(CO)_4\}]$ (2): A solution of Cp^*GaCl_2 (0.138 g, 0.5 mmol) in 15 mL THF was slowly added at −78 °C to a solution of $K[Co(CO)_4]$ (0.231 g, 1.1 mmol) in 15 mL THF. The solution was stirred for 14 h and was then allowed to warm to room temperature. Et_2O (2 mL) was added, and after two hours stirring the colour of the solution turned to red-brown and a white precipitate appeared. All volatiles were removed in vacuum, and

Table 1. Crystallographic data for **1−4**

	$1\cdot 2C_7H_8$	**2**	**$3\cdot OC_4H_8$**	**$4\cdot 2OC_4H_{10}$**
Empirical formula	$C_{28}H_{16}Co_4GaKO_{14}$	$C_{11}ClCo_3GaKO_{11}$	$C_{18}H_8Co_4GaLiO_{15}$	$C_{12}H_{20}Cl_6FeGa_2Na_2O_6$
M_r	920.95	629.17	776.62	714.25
T [K]	210(2)	200(1)	200(1)	190(1)
Crystal size	0.40 × 0.24 × 0.06	0.14 × 0.06 × 0.02	0.20 × 0.10 × 0.04	0.50 × 0.20 × 0.10
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
a [Å]	14.328(3)	9.777(2)	11.558(2)	13.427(3)
b [Å]	14.533(3)	15.587(3)	12.415(3)	16.778(3)
c [Å]	20.020(4)	13.594(3)	18.681(4)	12.675(3)
α [°]	101.85(3)	90	90	90
β [°]	94.79(3)	102.32(3)	90	108.61(3)
γ [°]	116.93(3)	90	90	90
V [Å^{-3}]	3562.5(12)	2024.0(7)	2680.5(9)	2706.2(9)
Z	4	4	4	4
d_c [g cm^{-3}]	1.717	2.065	1.924	1.753
μ_c [mm^{-1}]	1.431[c]	4.119[d]	1.154[c]	3.154[d]
2θ range [°]	$3.20 \leq 2\theta \leq 43.22$	$4.02 \leq 2\theta \leq 51.94$	$3.10 \leq 2\theta \leq 41.67$	$4.56 \leq 2\theta \leq 51.80$
hkl range	$-18 \leq h \leq 18$, $-17 \leq k \leq 19$, $-26 \leq l \leq 26$	$-10 \leq h \leq 11$, $-14 \leq k \leq 19$, $-16 \leq l \leq 16$	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-23 \leq l \leq 21$	$-16 \leq h \leq 16$, $-19 \leq k \leq 20$, $-14 \leq l \leq 15$
Data/restraints/parameters	15978/1/864	3799/0/253	5691/0/352	5142/0/266
No. of unique data	15978 (R_{int} = 0.0383)	3799 (R_{int} = 0.0387)	5691 (R_{int} = 0.0592)	5142 (R_{int} = 0.0779)
Independent reflections [$I > 2\sigma(I)$]	11045	2920	4553	3655
Goodness-of fit on F^2	1.006	0.913	1.013	0.901
R_1[a], wR_2[b] [$I > 2\sigma(I)$][a]	0.0411, 0.0965	0.0274, 0.0610	0.0377, 0.0727	0.0346, 0.0748
R_1[a], wR_2[b] [all data]	0.0687, 0.1081	0.0416, 0.0642	0.0574, 0.0790	0.0549, 0.0799
Largest diff. peak/hole [e·Å^{-3}]	0.806, −0.408	0.340, −0.745	0.447, −0.392	0.428, −0.727

[a] $R = \Sigma|F_0| - |F_c|/\Sigma|F_0|$. [b] $wR_2 = [\Sigma\omega(F_0^2 - F_c^2)^2]/[\Sigma(F_0^2)^2]^{1/2}$. [c] μ(Ag-K_α). [d] μ(Mo-K_α).

the oily residue was extracted with about 50 mL toluene. After filtration over silica gel, the volume of the solution was reduced to 2 mL and at −20 °C red-brown crystals of K[GaCl{$Co_2(CO)_6$}(μ-CO)}{$Co(CO)_4$}] (**2**) were obtained (177 mg, 60%). IR (KBr): $\tilde{\nu}$ = 2062(s) cm^{-1}, 2039(s), 1987(s), 1969(s), 1765(m) ν(CO).

[Li(THF)][Ga{$Co_2(CO)_6$(μ-CO)}$_2$] (3): A solution of [{$Co(CO)_4$}$_2$GaCl(THF)] (0.154 g, 0.3 mmol) in 5 mL toluene was slowly added at −78 °C to a slurry of LiCp* (0.063 g, 0.3 mmol) in 5 mL toluene. The reaction mixture was allowed to warm to room temperature and stirred for three days. After filtration over silica gel, the volume of the orange solution was reduced to 2 mL and at −30 °C orange crystals of [Li(THF)][Ga{$Co_2(CO)_6$(μ-CO)}$_2$] (**3**) were obtained (0.167 g, 70%). IR (KBr): $\tilde{\nu}$ = 1968(s) cm^{-1}, 1764(m) ν(CO). MS (ESI): m/z = 696 [M$^-$].

[Na(OEt_2)]$_2$[Fe(CO)$_4$($GaCl_3$)$_2$] (4): A solution of $GaCl_3$ (0.088 g, 0.5 mmol) in 5 mL Et_2O at 0 °C was slowly added to a suspension of Na_2[Fe(CO)$_4$] (0.216 g, 1 mmol) in 20 mL Et_2O. The colour changed to yellow, and after stirring for 3 h at room temperature, the colour changed again to yellow-red. Addition of *n*-hexane led to colourless crystals of [Na(OEt_2)]$_2$[Fe(CO)$_4$($GaCl_3$)$_2$] (**4**) (126 mg, 70%, based on $GaCl_3$). IR (KBr): 2082(s, br) cm^{-1}, 2042(s), 2035(s), 2025(s), 2000(m), 1978(s, br) ν(CO).

X-ray Structure Determination and Details of Refinement. Data were collected on a STOE IPDS area-detector diffractometer using Ag-K_α radiation (λ = 0.56087 Å) for complex **1** and Mo-K_α radiation (λ = 0.71069 Å) for **2**, **3** and **4**. Machine parameters, crystal data and data collection parameters are summarised in Table 1. The structures were solved by direct methods using SHELXS-86,[15a] and refined by full-matrix least-squares methods on F^2 in SHELXL-97[15b] with anisotropic displacement for non-H atoms (except for atom C50 of **1**, due to the limited crystal quality of this complex). Hydrogen atoms were placed in idealised positions and refined isotropically according to the riding model. The Flack-parameter of the chiral space group of **3** comes to −0.01(3).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-170990 (**1**), -170991 (**2**), -170992 (**3**) and -170993 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for comprehensive financial support. E. Leiner is grateful to the Fonds der Chemischen Industrie for a PhD fellowship.

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Received September 20, 2001
[I01371]