Solutions of Gallium Trichloride in Ethers: A ^{71}Ga NMR Study and the X-Ray Structure of $\text{GaCl}_3 \cdot \text{Monoglyme}$

Stefan Böck, Heinrich Nöth*, and Astrid Wietelmann

Institute of Inorganic Chemistry, University of Munich, Meiserstraße 1, D-8000 München 2

Dedicated to Prof. Dr. G. Fritz on the occasion of his 70th birthday

Z. Naturforsch. **45b**, 979–984 (1990); received January 22, 1990

^{71}Ga NMR Spectra, Gallium Trichloride-Ether, Gallium Trichloride-Tetrahydrofuran, *cis*-Dichloro-bis(dimethylglycolether)gallium-tetrachlorogallate

Solutions of GaCl_3 in various ethers have been studied by ^{71}Ga NMR spectroscopy. $\delta^{71}\text{Ga}$ data indicate that the predominant species in diethylether and tetrahydrofuran solutions are $\text{GaCl}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ and $\text{GaCl}_3 \cdot 2\text{OC}_4\text{H}_8$, respectively. However, in monoglyme solution dissociation occurs and the product crystallizing from the solution is [*cis*- $\text{GaCl}_2(\text{monoglyme})_2$]- GaCl_4 as demonstrated by an X-ray structure determination of the solvate $\text{GaCl}_3 \cdot \text{monoglyme}$.

Introduction

Aluminium trichloride, which crystallizes in an ionic lattice, dissolves in many polar solvents and forms a large number of coordination compounds. $[\text{Al}(\text{OH}_2)_6]\text{Cl}_3$ crystallizes from acid aqueous solutions of AlCl_3 [1]. The compound $\text{AlCl}_3 \cdot 2\text{CH}_3\text{CN}$ can be obtained from solutions of AlCl_3 in acetonitrile, and this compound was shown to be $[\text{Al}(\text{NCCH}_3)_5][\text{AlCl}_4] \cdot \text{CH}_3\text{CN}$ by X-ray structure determination [2]. In addition, a second acetonitrile adduct has been found to be $[\text{Al}(\text{NCCH}_3)_6][\text{AlCl}_4]_3$ [3]. Pyridine (py) yields several compounds with AlCl_3 depending on the mode of preparation, and the structures of $\text{AlCl}_3 \cdot 3\text{py}$ and $\text{AlCl}_3 \cdot 2\text{py}$ have been determined to be *mer*- $\text{AlCl}_3 \cdot 3\text{py}$ and [*trans*- $\text{Cl}_2\text{Al}(\text{py})_4$][AlCl_4], respectively [4]. From diethylether the compound $\text{AlCl}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, containing a tetracoordinated aluminium atom, has been isolated [5]. Moreover, two different kinds of $\text{AlCl}_3 \cdot 2\text{THF}$ compounds (THF = tetrahydrofuran) have been characterized. The first one results from the action of THF on the adduct $(\text{Me}_2\text{N})_3\text{SiCl} \cdot \text{AlCl}_3$. It is the molecular compound $\text{AlCl}_3 \cdot 2\text{THF}$ with a pentacoordinated Al-atom in a trigonal-bipyramidal environment and the THF molecules in apical positions [6]. In contrast, if toluene is added to a solution of AlCl_3 in tetrahydrofuran the solid $\text{AlCl}_3 \cdot 2\text{THF}$, which separates, is the ionic compound [*cis*- $\text{Cl}_2\text{Al}(\text{THF})_4$][AlCl_4] [7] whose existence was first

deduced from spectroscopic studies (IR, Raman, NMR) [8]. Dissociation of AlCl_3 in diethylether has been observed not only by the electrical conductance of its solution but also by ^{27}Al NMR spectroscopy [1, 9, 10]. Dissociation processes are increasingly favoured in the series diethylether, THF, dimethylglycolether (monoglyme), and dimethyldiglycolether [10]. Moreover, crown ethers support ionization, as shown by the complex of $2\text{AlCl}_3 \cdot 4\text{-crown-12}$ [11] producing the salt $[\text{Cl}_2\text{AlL}]\text{AlCl}_4$.

Many additional cations have been detected in solutions of AlCl_3 in highly polar solvents by ^{27}Al NMR spectroscopy. However, the question whether the solid in equilibrium with the solution reflects the solution state needs still further exploration. From this point of view it was of considerable interest to compare the behaviour of GaCl_3 towards ethers as solvents with that of AlCl_3 . Although ^{71}Ga NMR spectroscopy is not as versatile as ^{27}Al NMR spectroscopy, the method can be used to get information on solution species.

Results

Gallium trichloride in diethylether

The low melting adducts $\text{GaX}_3 \cdot \text{OEt}_2$ (X = Cl, Br, I) have been isolated and characterized [12], and it is well known that GaCl_3 dissolves much more readily in organic solvents than does AlCl_3 . In contrast to AlCl_3 solutions in diethylether those of GaCl_3 show only very weak electrical conductivity. 0.204 and 0.123 M solutions of GaCl_3 in diethylether are almost non-conducting, while the specific electrical conductivity of comparable

* Reprint requests to Prof. Dr. H. Nöth.

AlCl_3 solutions in diethylether is $1.2 \cdot 10^{-2} \text{ cm}^2 \Omega^{-1}$ [13]. Thus, GaCl_3 in diethylether appears to form almost no ionic products.

In consonance with these findings is the broad ^{71}Ga NMR signal at $\delta = 260$ ppm which we observe at much lower field than reported by Akitt *et al.* ($\delta^{71}\text{Ga} = 137$ ppm) [14]. This signal corresponds to the formation of $\text{Cl}_3\text{Ga} \cdot \text{OEt}_2$. Exchange of this etherate with solvent ether is slow as two sets of ^{13}C NMR signals are observed.

Gallium trichloride in tetrahydrofuran and dioxane

Tetrahydrofuran dissolves GaCl_3 quite readily. Solutions in the concentration range 0.12–0.97 mol/l show negligible electrical conductivity in contrast to AlCl_3 solutions in this solvent [15]. These solutions produced a detectable ^{71}Ga NMR signal neither at ambient temperature nor at lower temperature (-20°C). Also, the isolated $\text{GaCl}_3 \cdot \text{THF}$, dissolved in C_6D_6 , gave no ^{71}Ga resonance. Obviously, quadrupolar relaxation is very fast for this compound. As expected, two ^{13}C NMR signals are observed for $\text{GaCl}_3 \cdot \text{THF}$. The carbon atoms bonded to the oxygen atom are shifted to lower field compared with the free ligand while the carbon atoms of the other CH_2 groups are slightly better shielded. Broad resonances are observed for the two sets of CH_2 groups.

A ^{71}Ga NMR spectrum may allow to distinguish between tetra- or pentacoordination in solution. No ^{71}Ga NMR signal could be recorded for saturated solutions of GaCl_3 in dioxane. This definitely also excludes the formation of the readily detectable GaCl_4^- anion. This is ascertained by the very low electrical conductivity of the GaCl_3 solution in dioxane. In this respect, GaCl_3 behaves like AlCl_3 in dioxane, where a ^{27}Al NMR signal at $\delta = 66$ ppm points to the presence of pentacoordinated Al [17]. No signal at $\delta = 105$ ppm, typical for the presence of AlCl_4^- [17] was found. This excludes dissociation of AlCl_3 in dioxane into solvated AlCl_2^+ and AlCl_4^- .

Gallium trichloride in monoglyme and diglyme

Compared to solutions of GaCl_3 in diethylether or tetrahydrofuran the solubility of this halide in monoglyme is low (<0.1 M). This is one of the reasons why no ^{71}Ga NMR signal was recorded. In contrast, a 0.34 M solution of GaCl_3 in diglyme

exhibits two ^{71}Ga NMR signals, a broad and relatively weak signal at $\delta = 329$ ppm and a strong and fairly sharp one at $\delta = 261$ ppm. On dilution, the broad resonance vanishes while the other becomes increasingly sharper (260 *versus* 160 Hz at half height). These results clearly indicate dissociation of GaCl_3 , presumably according to

The ^{71}Ga NMR chemical shift ($\delta = -329$ ppm) corresponds best with tetracoordination: both a pentacoordinated as well as hexacoordinated gallium center should show a resonance at much higher field [17]. We therefore assign this signal to a tetracoordinated $\text{GaCl}_3 \cdot \text{L}$ adduct. Whether dissociation occurs according to eq. (1) or (2) cannot be decided on the basis of the ^{71}Ga NMR spectra alone.

The structure of $[\text{GaCl}_2(\text{monoglyme})_2]\text{GaCl}_4$

The adduct $\text{GaCl}_3 \cdot \text{monoglyme}$ separating from monoglyme solutions forms well shaped crystals from dichloromethane solutions suitable for an X-ray crystallographic study. The crystals are orthorhombic, and 8 $\text{GaCl}_3 \cdot \text{monoglyme}$ units are found in the unit cell. However, as depicted in Fig. 1 the compound is not a molecular adduct but rather the salt $[\text{Cl}_2\text{Ga}(\text{monoglyme})_2]\text{GaCl}_4$. Bonding parameters are summarized in Table I.

The tetrachlorogallate anion deviates only slightly from a regular tetrahedron, the Cl–Ga–

Fig. 1. ORTEP plot of $[\text{Cl}_2\text{Ga}(\text{monoglyme})_2]\text{GaCl}_4$. Thermal ellipsoids represent a 30% probability.

Table I. Selected bond distances (in Å) and bond angles (in degrees) of $[\text{GaCl}_2(\text{monoglyme})_2]\text{GaCl}_4$. Estimated standard deviations in parenthesis.

Bond distances			
Ga1–Cl2	2.187(2)	Ga2–O8	2.064(8)
Ga1–Cl2	2.177(2)	Ga2–O11	2.081(6)
Ga1–Cl3	2.171(2)	O2–C1	1.365(18)
Ga1–Cl4	2.170(2)	O2–C3	1.540(9)
Ga2–Cl5	2.204(5)	O5–C6	1.435(12)
Ga2–Cl6	2.223(4)	O5–C4	1.437(15)
Ga2–O5	2.039(9)	O8–C7	1.502(12)
Ga2–O2	2.093(5)	O11–C12	1.496(17)
Bond angles			
Cl1–Ga1–Cl2	110.4(1)	Cl5–Ga2–O5	96.4(3)
Cl1–Ga1–Cl3	110.1(1)	Cl6–Ga2–O5	94.1(3)
Cl2–Ga1–Cl3	109.0(1)	O2–Ga2–O5	96.4(3)
Cl3–Ga1–Cl4	109.0(2)	Cl5–Ga2–O8	97.0(3)
Cl2–Ga1–Cl4	110.2(2)	Cl6–Ga2–O8	96.4(3)
Cl3–Ga1–Cl4	109.0(2)	O2–Ga2–O8	84.0(3)
Cl5–Ga2–Cl6	101.1(1)	O5–Ga2–O8	161.0(3)
Cl5–Ga2–O2	168.0(2)	Cl5–Ga2–O11	91.9(2)
Cl6–Ga2–O2	90.7(2)	Cl6–Ga2–O11	166.7(2)

Cl bond angles ranging from 108.1(1) to 110.4(1) and the Ga–Cl bond lengths from 2.170(2) to 2.187(2) Å.

The cationic part of the structure is more interesting, the most notable feature being the *cis*-orientation of the chlorine atoms at the hexacoordinated gallium center. Consequently, the average GaCl distance (2.213 Å) is larger than in the tetra-coordinated GaCl_4^- anion (2.176 Å), in spite of the positive charge in the cation.

Due to the small OGaO bite angles of the monoglyme ligand (80.1(3) and 78.9(3)° respectively), a strong distortion from regular octahedral symmetry is noted, the cations local symmetry approaching the point group symmetry C_2 with the two-fold axis bisecting the ClGaCl angle (101.1(1)°). The transoid bond angles also deviate strongly from the ideal 180°. Respective values are Cl5–Ga2–O2 168.0(2)°, Cl6–Ga2–O11 166.7(2)°, and O5–Ga2–O8 161.0(3)°.

Discussion

The formation of coordination complexes of gallium trihalides, and GaCl_3 in particular, is well known [12]. $\text{GaCl}_3 \cdot \text{OEt}_2$ has been isolated as a low melting solid (m.p. 16 °C) and its molecular constitution established by vibrational spectroscopy. The value $\delta^{71}\text{Ga} = 137$ ppm, as observed for the

neat liquid fits, with tetracoordination [14]. The ^{71}Ga NMR signal for solutions of GaCl_3 in diethylether is found at lower field ($\delta = 260$ ppm); this chemical shift value would correspond with the formation of GaCl_4^- [17]. The line width (≈ 7500 Hz), however, excludes such an assignment, as does the low electrical conductivity. Therefore, we have to conclude that the principal species in solution is $\text{GaCl}_3 \cdot \text{OEt}_2$.

In contrast to AlCl_3 , gallium trichloride seems not to form a stable $\text{GaCl}_3 \cdot 2\text{THF}$ adduct. $\text{GaCl}_3 \cdot \text{THF}$ was isolated from THF solutions, and neither a solution of this compound in benzene nor in tetrahydrofuran allowed the detection of a ^{71}Ga NMR signal. This observation falls in line with the higher stability of $\text{AlCl}_3 \cdot 2\text{NMe}_3$ as compared to $\text{GaCl}_3 \cdot 2\text{NMe}_3$ [18]. However, one might expect the formation of $\text{GaCl}_3 \cdot 2\text{THF}$ since GaCl_3 reacts with dioxane, to produce a 1:1 adduct containing pentacoordinated gallium [16]. The asymmetric electron distribution around gallium in such complexes may generate a strong field gradient allowing rapid relaxation and preventing the observation of a ^{71}Ga NMR signal. Moreover, AlCl_3 is a stronger Lewis acid for hard bases [19], and this may be an additional factor causing AlCl_3 to dissociate appreciably in THF solution, from which $[\text{trans-Cl}_2\text{Al}(\text{THF})_4]\text{AlCl}_4$ can be isolated [7]. Dissociation of this type occurs with GaCl_3 only in polyether solutions as shown here.

However, in the salt $[\text{Cl}_2\text{Ga}(\text{monoglyme})_2]\text{GaCl}_4$ the chlorine atoms are in a *cis*-position in contrast to $[\text{trans-Cl}_2\text{Al}(\text{THF})_4]^+$ [7]. Reasons advanced for this different arrangement remain tentative and any further discussion should be postponed until the structure of $[\text{Cl}_2\text{Al}(\text{monoglyme})_2]^+$ has been established.

The *cis*-arrangement is also found in $[\text{Cl}_2\text{Ga}(\text{dipy})_2]^+$, a cation possessing two chelating ligands [19], while the chlorine atoms in $[\text{Cl}_2\text{Ga}(\text{py})_4]^+$ are in *trans*-position [20]. The structural difference between $[\text{Cl}_2\text{Ga}(\text{dipy})_2]^+$ and $[\text{Cl}_2\text{Ga}(\text{py})_4]^+$ has been explained by steric interactions of the hydrogen atoms next to the nitrogen atom. In $[\text{cis-Cl}_2\text{Ga}(\text{dipy})_2]^+$ this interaction is avoided. Similarly, the $[\text{trans-Cl}_2\text{Ga}(\text{py})_4]^+$ geometry is possible due to rotation of the pyridine molecules around the GaN bonds in order to minimize H–H interactions of the hydrogen atoms in *ortho*-position. Arguments of this kind are, however, not

fully valid for monoglyme as a ligand due to the flexibility of its O_2C_2 skeleton.

The GaCl bond lengths in *cis*- Cl_2GaL_4 cations are shorter than those in *trans*- $Cl_2GaL_4^+$ species (2.213 Å in $[Cl_2Ga(monoglyme)_2]^+$, 2.265 Å in $[Cl_2Ga(dipy)_2]^+$ and 2.31 Å in $[trans-Cl_2Ga(py)_4]^+$).

A comparison of the GaO bond distances for $Cl_2Ga(monoglyme)_2^+$ (average 2.069 Å) with those in pentacoordinated $GaCl_3 \cdot 1,4$ -dioxane (2.21 Å) [16] and $Ga_2Cl_4 \cdot 1,4$ -dioxane (2.03 Å) [21], where the dioxane acts as a monodentate ligand, shows a violation of the general rule that the respective bond lengths should increase as the coordination number increases. We attribute the comparatively short average GaO bonds in $[Cl_2Ga(monoglyme)_2]^+$ to the positive charge associated with this species. The GaO bonds *trans* to chlorine are longer than the other two, indicating an electronic effect.

Experimental

Solvents were purified by several fractional distillations under dry dinitrogen, dried with appropriate reagents (mostly $LiAlH_4$), distilled and stored under N_2 . $GaCl_3$ was prepared from the elements and sublimed prior to use. All experiments were performed in flame dried, nitrogen filled apparatus.

Electrical resistance was measured using a conductance bridge as supplied by Technische Werkstätten Weilheim. The cell constant was determined as $Z = 0.65 \text{ cm}^2$, and the conductivity calculates as $\Lambda = 1000 \cdot Z/(R \cdot c)$.

NMR spectra were recorded with a Bruker WP 200 spectrometer operating at 61.0033046 MHz for ^{71}Ga , pulse angle $15 \mu s$, sweep width 20,000 Hz, offset 10,000 Hz, and a synthesizer frequency varying for 55.8–65.5 MHz. 1H and ^{13}C NMR spectra were measured under standard conditions. C_6D_6 was used as lock and internal standard. Standards were *t*TMS for 1H and ^{13}C , and 1 M $Ga(OH_2)_6^{3+}$ for ^{71}Ga .

Galliumtrichloride-diethylether

Ether (2.5 ml) was cooled to $0^\circ C$ and 90 mg of $GaCl_3$ (0.51 mmol) were added with stirring. The solution obtained at ambient temperature was 0.204 M. It was diluted by distilling measured volumes of ether into the $GaCl_3$ solution. Clear solutions were obtained which turned brown on prolonged standing at ambient temperature. NMR: $\delta^{13}C$ (ppm): 66.6 (3.3%), 65.9, 15.9 (3.3%), 15.2.

The signals at 66.6 and 15.9 result from $GaCl_3 \cdot OEt_2$ the others from the solvent, $\delta^{71}Ga$ (ppm): 260, $h(1/2) = 2700 \text{ Hz}$. Equivalent conductivity at $18^\circ C$: $<1.2 \cdot 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ for 0.204 and 0.123 M solutions.

Galliumtrichloride-tetrahydrofuran

a) 3.0 ml of tetrahydrofuran (42 mmol) were cooled to $0^\circ C$. 520 mg of $GaCl_3$ (2.9 mmol) were then added with stirring. A clear solution resulted which was immediately used. Equivalent conductivity of the solution (0.97 M, 0.137 M) at $20^\circ C$: $<1.7 \cdot 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. No ^{71}Ga NMR signal was observed. δ^1H (C_6D_6 , ppm): 3.60 (m, 2H), 1.64 (m, 2H).

b) At $-10^\circ C$ 560 mg of $GaCl_3$ (3.21 mmol) were dissolved in 15 ml of pentane. To this stirred solution was added 2.5 ml of tetrahydrofuran. A solid precipitated immediately, which was filtered off, washed with 10 ml cold pentane and dried *in vacuo*. Yield: 620 mg $GaCl_3 \cdot OC_4H_8$ (79.5%), m.p. $72-74^\circ C$.

$C_4H_8Cl_3GaO$ (248.2)

Calcd	C 19.36	H 3.25	Cl 43.85,
Found	C 17.74	H 3.34	Cl 42.92.

1H NMR (in C_6D_6 , ppm): 3.52 (broad, m, 2H), 1.00 (broad, m, 2H); ^{13}C NMR (in C_6D_6 , ppm): 72.9, 24.5; ^{71}Ga NMR: no signal observed.

Galliumtrichloride-dimethylglycoether

$GaCl_3$ (460 mg, 2.64 mmol) was cooled to $-40^\circ C$ and 5.0 ml (41.3 mmol) of the ether added. While stirring, the mixture was allowed to attain ambient temperature. On heating shortly to $\approx 80^\circ C$, a clear solution resulted which on cooling to ambient temperature provided a white, insoluble product. This was isolated and recrystallized from CH_2Cl_2 . Clear, well shaped prisms separated. Yield: 350 mg (52%), m.p. $140-145^\circ C$.

$C_4H_{10}Cl_3GaO_2$ (266.1)

Calcd	Cl 39.96,
Found	Cl 39.50.

The crystals proved to be $[cis-Cl_2Ga(CH_3OCH_2CH_2OCH_3)_2]GaCl_4$ (v.i.).

IR: prominent bands (cm^{-1}) at 3100–2920 (νCH_2 , CH_3), 1420–1460 (δCH_2 , CH_3), 820 (νGaO_2), 365 broad ($\nu GaCl_4^-$, $\nu GaCl_2^+$).

Galliumtrichloride-1,4-dioxane

Two solutions were prepared at $0^\circ C$: 100 mg $GaCl_3$ in 3.0 ml $C_4H_8O_2$ (0.17 M) and 630 mg $GaCl_3$ in 12.0 ml $C_4H_8O_2$ (0.3 M). None of these

showed a ^{71}Ga NMR signal. $\delta^{17}\text{O}$: The signal was shifted from -6.0 (free dioxane) to 0.02 ppm ($h(1/2) = 120$ Hz), indicating solvent exchange as supported by ^{13}C NMR data: $\delta = 67.0$ ppm for the 0.3 M and 0.17 M solution.

Galliumtrichloride-dimethyldiglycolether

300 mg of GaCl_3 (1.7 mmol) were dissolved in 5.0 ml of the ether as described for the dimethylglycolether. A clear solution resulted on warming to ambient temperature.

$\delta^{71}\text{Ga}$ data were recorded as follows:

c (mol/l)	0.34	0.17	0.085	0.057	0.031
$\delta^{71}\text{Ga}$	261.4	260.8	260.8	260.9	261.2
	(260) ^a	(140) ^a	(140) ^a	(140) ^a	(160) ^a
	329.6 ^{b,c}				

^a Line width; ^b very broad; ^c ratio of the two signals: $\approx 5:1$.

X-Ray structure determination

Single crystals from CH_2Cl_2 solution. Syntex R3 diffractometer operating with MoK_α radiation ($\lambda = 0.71069$ Å), graphite monochromator, crystal size: $0.25 \times 0.3 \times 0.43$ mm. Temperature: 193 K. $\text{C}_8\text{H}_{20}\text{Cl}_6\text{Ga}_2\text{O}_4$, $M_r = 532.2$, $a = 14.950(4)$, $b = 6.807(2)$, $c = 19.400(5)$ Å, $V = 1974.1(8)$ Å³, $Z = 4$, $d_{\text{calc}} 1.791$ g/cm³, space group $\text{Pca}2_1$, No. 29 (Int. Tables), $F(000) = 1056$, $\mu = 3.355$ mm⁻¹. Data Collection: ω -scan, scan width 1.0° , scan to background ratio: $1:0.5$, variable scan speed 1.6 – $29.3^\circ/\text{min}$, 2θ -range: 3 – 50° in $+h+k+/-l$, the intensity of two check reflections was measured after every 48 data, 3719 reflections collected; empirical absorption correction with 10 ψ -scans in the 2θ -range 8 – 48° , max./min. transmission: $0.297/0.039$. Data reduction with Lp- and absorption correction. 2597 unique reflection, of which 2375 were considered as observed ($3\sigma(I)$). Structure solution: Patterson and Fourier methods, refinement of non-hydrogen atoms anisotropically, H-atom positions in calculated positions. Final $R = 0.0518$, $R_w = 0.0535$ with $1/w = \sigma^2(F) + 0.0384(F)^2$; 192 parameters refined, GOOF = 0.962 ; largest residual electron density: 1.6 e/Å³ (close to Ga).

Table II. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{eq} (Å² $\times 10^3$) of the non-hydrogen atoms of $[\text{Cl}_2\text{Ga}(\text{monoglyme})_2]\text{GaCl}_4$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U
Ga(1)	5338(1)	3208(1)	3273	37(1)*
Ga(2)	7495(1)	183(1)	775(1)	27(1)*
Cl(1)	6700(1)	4376(2)	3273(2)	50(1)*
Cl(2)	4615(2)	4204(4)	4182(1)	67(1)*
Cl(3)	4630(2)	4181(4)	2357(1)	61(1)*
Cl(4)	5419(2)	25(2)	3263(3)	53(1)*
Cl(5)	6448(3)	2251(6)	1112(2)	53(2)*
Cl(6)	8554(3)	2247(5)	426(2)	48(2)*
C(1)	9189(11)	−2279(23)	495(7)	51(6)*
O(2)	8276(4)	−2221(5)	475(2)	25(2)*
C(4)	7587(8)	−1560(18)	−564(5)	86(6)*
C(3)	7906(7)	−3092(12)	−200(3)	55(4)*
O(5)	7002(7)	−267(12)	−192(4)	37(3)*
C(7)	8379(8)	1256(12)	2191(4)	59(4)*
C(6)	6615(7)	1391(13)	−537(4)	51(3)*
O(8)	8031(7)	−359(11)	1737(3)	33(3)*
C(9)	7480(5)	−1587(10)	2182(3)	28(3)*
C(10)	7120(6)	−3140(9)	1639(4)	37(3)*
O(11)	6740(5)	−2228(8)	1087(2)	39(2)*
C(12)	5744(11)	−2314(23)	1022(9)	53(6)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The remaining electron density map was featureless. The U_{ij} values for atoms C4 (in particular) C6, C7, C12 show at least one fairly large U_{ij} value. And, indeed some of the CO and CC bond lengths are shorter than expected. The U_{ij} values suggest some disorder, but we could not improve the results by using a split model. All calculation were performed using the SHELXTL programme package, version 4.0, Nicolet Corp. Atomic coordinates are summarized in Table II. Further details on the structure determination can be obtained from Gesellschaft für wissenschaftlich-technische Information mbH, Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, by quoting the number CSD 54468, the name of the authors, and the literature citation.

We thank Deutsche Forschungsgemeinschaft and Chemetall GmbH for support of this work.

- [1] M. J. Taylor, in G. Wilkinson (ed.): *Comprehensive Coordination Chemistry*, **Vol. 3**, p. 105, Pergamon Press, New York, London (1987).
- [2] I. R. Beattie, P. J. Jones, J. A. K. Howard, L. E. Smart, J. J. Gilmore, and J. W. Akitt, *J. Chem. Soc. Dalton Trans.* **1979**, 528; M. Dalibart, J. Deroualt, M. T. Forel, and P. Caillet, *J. Mol. Struct.* **63**, 233 (1980).
- [3] M. Dalibart, M. Fouassier, and M. T. Forel, *J. Mol. Struct.* **36**, 7 (1977).
- [4] P. Pullman, K. Hensen, and J. W. Bats, *Z. Naturforsch.* **37b**, 1312 (1982).
- [5] P. J. Ogren, J. P. Cannon, and C. F. Smith (Jr.), *J. Phys. Chem.* **75**, 282 (1971).
- [6] A. H. Cowley, M. C. Cushner, R. E. Davies, and P. E. Riley, *Inorg. Chem.* **20**, 1179 (1981).
- [7] N. C. Means, C. M. Means, S. G. Bott, and J. L. Atwood, *Inorg. Chem.* **26**, 1463 (1987).
- [8] J. Deroualt and M. T. Forel, *Inorg. Chem.* **16**, 3207 (1977); J. Deroualt, P. Granger, and M. T. Forel, *ibid.* **16**, 3214 (1977).
- [9] P. Wolfgardt, Diploma Thesis, University of Munich (1972).
- [10] H. Nöth, R. Rurländer, and P. Wolfgardt, *Z. Naturforsch.* **37**, 29 (1982).
- [11] J. J. Atwood, H. Elgamel, G. H. Robinson, S. G. Bott, J. A. Weeks, and W. E. Hunter, *Inclus. Phenomena* **2**, 367 (1984).
- [12] H. Ishihara and H. Negita, *Bull. Chem. Soc. Jpn.* **58**, 2731 (1985).
- [13] Yu. M. Kessler, N. M. Alpastova, and O. R. Osipov, *Russ. Chem. Rev.* **33**, 126 (1964).
- [14] J. W. Akitt, N. N. Greenwood, and A. Storr, *J. Chem. Soc.* **1965**, 4410.
- [15] G. G. Evans, T. R. P. Gibb (Jr.), J. K. Kennedy, and F. P. Del Greco, *J. Am. Chem. Soc.* **76**, 4861 (1954).
- [16] A. Boardman, S. E. Jeffs, R. W. H. Small, and I. J. Worral, *Inorg. Chim. Acta* **87**, L27 (1984).
- [17] R. K. Harris and B. E. Mann (eds.), *NMR and the Periodic Table*, Academic Press, London, New York, San Francisco (1978).
- [18] I. R. Beattie, T. Gilson, and G. A. Ozin, *J. Chem. Soc. A* **1968**, 1092.
- [19] R. Revisto and G. J. Dalenik, *J. Chem. Soc. Dalton Trans.* **1977**, 341.
- [20] I. Sinclair, R. W. H. Small, and I. J. Worral, *Acta Crystallogr.* **B37**, 1290 (1981).
- [21] J. C. Beanish, R. W. H. Small, and I. J. Worral, *Inorg. Chem.* **18**, 220 (1978).