Diazenato- und des Hydrazido-Liganden unterscheiden sich. Sie entsprechen dabei den Valenzschreibweisen Mo=N=N—C=O (Diazenato-Ligand) bzw. Mo—N—N=C—O—(Mo) (Hydrazido-Ligand). Ein besonders charakteristischer Unterschied besteht im N—N- Abstand dieser Liganden. Er beträgt im Diazenato-Ligand [N(1)—N(2)] 1,271 (3) Å und im Hydrazido(1 −)-Ligand [N(4)—N(5)] 1,465 (3) Å. Diazenato- und Hydrazido(1 −)-Liganden sind sehr wahrscheinlich Zwischenstufen bei der enzymatischen Stickstoff-Fixierung. Beide Wasserstoffatome des Hydrazido(1 −)-Liganden befinden sich eindeutig am endständigen Stickstoffatom N(4). Die Bindungsparameter des Hydroxylaminato-Liganden zeigen keine Besonderheiten. Zwischen den beiden Molybdänatomen besteht keine Wechselwirkung. Sie besitzen formal die Oxidationszahl + IV. Der Mo—Mo-Abstand beträgt 3,408 (1) Å.

Die Titelverbindung ist das erste strukturell charakterisierte Beispiel für die chelatartige Bindung eines Hydrazido(1 −)-Liganden, der über keine Thiocarbonyl-Gruppe verfügt. Von Acyl-Hydrazinen abgeleitete Hydrazido-Liganden sind üblicherweise '*side on*' (Mattes, Scholand, Mikloweit & Schrenk, 1987*b*) oder '*end on*' gebunden (Fitzroy, Frederiksen, Murray & Snow, 1985).

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A Structural Study of Trichloro(tetrahydrofuran)iron(III)

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Abstract. Trichloro(tetrahydrofuran)iron(III), $[Fe(Cl)_3(C_4H_8O)]$, $M_r = 234{\cdot}3$, monoclinic, $P2_1/m$, $a = 6{\cdot}288$ (1), $b = 10{\cdot}360$ (2), $c = 7{\cdot}477$ (2) Å, $\beta = 106{\cdot}05$ (2)°, $V = 468{\cdot}1$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}662$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 24{\cdot}071$ cm^{-1}, $F(000) = 234$, $T = 292$ K, $R = 0{\cdot}051$ for 790 ($F_o^2 > 3\sigma F_o^2$) reflections. The molecule has tetrahedral stereochemistry, with a crystallographic mirror plane. The average Fe—Cl distance is 2·154 [2] Å, where [ ] signify the e.s.d., *viz.* $[(\sum\Delta_i^2)/n(n-1)]^{1/2}$. The average Cl—Fe—Cl and Cl—Fe—O angles are 112·6 [11] and 106·7 [9]°, respectively.

Introduction. While many transition-metal chlorides are too insoluble to be used effectively as starting materials in syntheses, they can first be converted to their tetrahydrofuran (THF) adducts, which are then synthetically useful (Fackler, 1982). This is particularly true of metal trichlorides, and for several of these the THF adducts are of the general formula MCl$_3$(THF)$_3$. The crystal structures of the following have been reported: MCl$_3$(THF)$_3$, M = Sc, Ti, V and Cr (Cotton, Duraj, Powell & Roth, 1986, and references therein).

We and others (Walker & Poli, 1989*a*) have recently been interested in the formation of phosphine complexes of iron(III) and, accordingly, contemplated the use of a FeCl$_3$(THF)$_n$ compound as a starting material. The literature contains a description of one such compound, the monoadduct, FeCl$_3$(THF) (Benner & Root, 1972). Out of curiosity about the authenticity of this claim, we have prepared the compound and determined its structure. It is obtainable in exactly the manner described and is, indeed, a tetrahedral, molecular compound.

Experimental. The complex was prepared by the published procedure (Benner & Root, 1972) and crystals suitable for X-ray study were obtained by sublimation. One of irregular geometry of dimen-

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Table 1. *Positional parameters for* $FeCl_3(THF)$ *with e.s.d.'s in parentheses*

The equivalent isotropic thermal parameter is $1/3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

	x	y	z	B_{eq} (Å^2)
Fe	0·06584 (9)	0·250	0·37589 (9)	4·64 (1)
Cl(1)	−0·2583 (2)	0·250	0·4206 (2)	7·58 (4)
Cl(2)	0·1258 (2)	0·0764 (1)	0·2392 (2)	8·20 (3)
O	0·2807 (5)	0·250	0·6193 (5)	5·37 (8)
C(1)	0·3793 (7)	0·3669 (4)	0·7225 (7)	9·2 (1)
C(2)	0·509 (1)	0·3199 (5)	0·9051 (6)	9·7 (1)

Table 2. *Selected bond distances* (Å) *and valence angles* (°) *for* $FeCl_3(THF)$ *with e.s.d.'s in parentheses*

Fe—O	1·944 (3)	O—C(1)	1·477 (5)
Fe—Cl(1)	2·155 (2)	C(1)—C(1)	1·468 (7)
Fe—Cl(2)	2·152 (1)	C(2)—C(2)′	1·449 (8)
Cl(1)—Fe—Cl(2)	111·78 (4)	Fe—O—C(1)	124·9 (2)
Cl(1)—Fe—O	107·3 (1)	C(1)—O—C(1)′	110·1 (3)
Cl(2)—Fe—Cl(2)′	113·32 (6)	O—C(1)—C(2)	105·1 (4)
Cl(2)—Fe—O	106·07 (6)	C(1)—C(2)—C(2)′	109·4 (4)

sions 0·50 × 0·30 × 0·25 mm was mounted in a capillary tube. Cell constants were derived from least-squares refinement based on 25 reflections having $25 < 2\theta < 35°$. Intensity data were collected at a constant scan rate with a variable number of scans (maximum = 6), which was determined on the basis of optimum counting statistics $[F/\sigma(F) = 30]$, using the moving-crystal/moving-counter technique with $0 < 2\theta < 55°$ (h = 0 to 8, k = 0 to 13, l = −10 to 10) on a Rigaku AFC5R diffractometer using graphite-monochromated Mo$K\alpha$ radiation. Three standard reflections ($34\bar{1}$, $33\bar{2}$, $\bar{1}3\bar{3}$), measured every 250 reflections, showed some (6%) decay. Data were corrected for decay, Lorentz and polarization effects, and for absorption effects based on ψ scans using the empirical method of North, Phillips & Matthews (1968); T_{min} = 0·6000, T_{max} = 1·000. 1137 data were collected and averaged to 790 unique, observed reflections ($F_o^2 > 3\sigma F_o^2$); $R_{merge}(F_o)$ = 0·082. Scattering factors, including anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). Systematic absences from the data indicated that the space group was either $P2_1/m$ or $P2_1$. An $N(Z)$ test suggested a centrosymmetric structure, and the $P2_1/m$ space group was selected and later proved to be correct by the successful refinement. All computations were carried out using the *SDP/V*, V3.0 package of programs (B. A. Frenz & Associates Inc., 1985). The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement. All non-H atoms were refined with anisotropic thermal parameters. All the H atoms were located in a difference map and their thermal parameters constrained to one value which together with their positions was refined. $wR = \{[\sum w(|F_o| - |F_c|)^2]/[\sum w(F_o)^2]\}^{1/2}$ was minimized, where $w = 1/\sigma^2(|F_o|)$ and σ is the standard deviation in a single measurement; the final R value was 0·0506, wR = 0·0642 and S = 1·508 for 59 variables. The largest shift/e.s.d. in the final least-squares cycle was 0·36; the maximum and minimum residual electron densities in the final difference Fourier map were 0·50 and −0·47 e Å^{-3}, respectively.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Table 1.* Bond distances and angles are given in Table 2. An *ORTEP* (Johnson, 1965) drawing of the molecule is presented in Fig. 1, together with the numbering scheme used.

The structure, as shown in Fig. 1, is clearly tetrahedral. One Cl, the Fe and the O atoms of the THF molecule reside on a mirror plane. There is no apparent crystallographic disorder in the THF ligand. The angle between the C(1)OC(1)′ plane and the C(1)C(2)C(2)′C(1)′ plane is 9·9 (12)°.

Walker & Poli have recently reviewed Fe—Cl distances (Walker & Poli, 1989*a*). They are in the range 2·175–2·185 Å in various salts. It is 2·154 [2] Å here. A shorter distance (by *ca* 0·025 Å) is understandable since one Cl^- is replaced by the O of THF.

It is interesting that although neutral four-coordinated complexes of Fe^{III} are common, such as $FeCl_3(THF)$, $FeCl_3(R_2O)$ (R = Me, EtO),

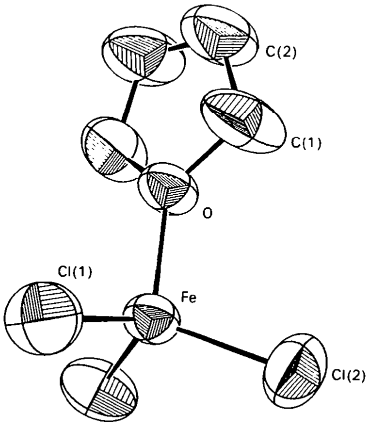

Fig. 1. An *ORTEP* drawing of $FeCl_3(THF)$ showing a partial atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

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* Lists of structure factors, anisotropic displacement parameters, a stereoview of the unit-cell packing and full tables of positional parameters, bond distances and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52804 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$FeCl_3(POCl_3)$, $2FeCl_3.[MeSe(CH_2)_3SeMe]$, and $FeCl_3(PR_3)$ (R = Ph, cyclohexyl), these varied complexes have not been previously characterized structurally (Walker & Poli, 1989*b*, and references therein). The structure of $[ZnCl(C_4H_8O)(\mu\text{-}Cl)]_\infty$ has been reported (Bottomley, Ferris & White, 1989).

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Structures of 2,2,2,2,2-Pentaammine-1-aqua-1,2-(μ-imidazolato-*N*,*N'*)-1-(iminodiacetato-*O*,*O'N*)cobalt(III)copper(II) Perchlorate Trihydrate and 2,2,2,2,2,3,3,3,3,3-Decaammine-1,2;1,3-di-(μ-imidazolato-*N*,*N'*)-1-(iminodiacetato-*O*,*O'*,*N*)dicobalt(III)copper(II) Perchlorate Tetrahydrate

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Abstract. Complex (I): $[(C_4H_5NO_4)(H_2O)Cu(\mu\text{-}C_3H_3N_2)Co(NH_3)_5](ClO_4)_2.3H_2O$, $M_r = 676·7$, monoclinic, $P2_1/c$, $a = 13·024\,(2)$, $b = 15·400\,(2)$, $c = 13·198\,(4)$ Å, $\beta = 111·28\,(2)°$, $V = 2466·5$ Å^3, $Z = 4$, $D_x = 1·822$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0·71070$ Å) = 18·4 cm^{-1}, $F(000) = 1388$, $T = 298$ K, $R = 0·062$ for 2859 significant reflections. Cu^{II} and Co^{III} are bridged by Im (imidazolate). Cu^{II} shows a square-pyramidal coordination by two N atoms and two O atoms of Ida (iminodiacetate) and Im in the equatorial plane, and by a water on the axis. Complex (II): $[(NH_3)_5Co(\mu\text{-}C_3H_3N_2)Cu(C_4H_5NO_4)(\mu\text{-}C_3H_3N_2)\text{-}Co(NH_3)_5](ClO_4)_4.4H_2O$, $M_r = 1086·8$, monoclinic, $P2_1/n$, $a = 15·617\,(2)$, $b = 8·876\,(1)$, $c = 28·801\,(4)$ Å, $\beta = 105·42\,(1)°$, $V = 3848·8$ Å^3, $Z = 4$, $D_x = 1·876$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0·71070$ Å) = 17·66 cm^{-1}, $F(000) = 2228$, $T = 298$ K, $R = 0·073$ for 2440 significant reflections. Two Im anions connect two Co^{III} atoms to one Cu^{II} atom forming a heterotrinuclear complex. The Cu^{II} also shows a square-pyramidal coordination by three N atoms and one O atom of Ida and Im in the equatorial plane and another O atom of Ida on the axis. The plane of Ida is somewhat distorted.

Introduction. At the active site of superoxide dismutase (SOD) Cu^{II} and Zn^{II} are bridged by an imidazolate (Im) anion (deprotonated imidazole) and the Cu^{II} atom shows a distorted square-pyramidal coordination, being bonded to four N atoms and one O atom (Tainer, Getzoff, Beem, Richardson & Richardson, 1982). In order to find out the relationship between the activity and the configuration of SOD, a series of Im-bridged heteronuclear complexes have been synthesized and crystallized. As part of our research programme, we now report the crystal structures of the two title Im-bridged heteronuclear complexes.

Experimental. Complex (I): small green block crystals from a water solution. Accurate cell dimensions were determined on a CAD-4 diffractometer by least-squares treatment of the setting angles of 25 reflections in the range $14·4 < \theta < 16·8°$. Crystal dimensions $0·15 \times 0·15 \times 0·15$ mm; intensities of reflections with indices h −15 to 15, k 0 to 18, l 0 to 15, with $0 < 2\theta < 50°$ were measured; ω–2θ scans; ω-scan width $(0·80 + 0·35\tan\theta)°$, graphite-monchromated Mo $K\alpha$ radiation. Intensities of three

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