

APPENDIX

Correlation between atom coordinations and compound stoichiometry

The crystal-chemical formulae of ternary compounds $R_xT_yM_z$ can be written in a general form (Lima-de-Faria, Hellner, Makovicky, Liebau & Parthé, 1990) as

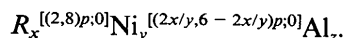
$$R_x^{[r_T, r_M; r_R]} T_y^{[t_R, t_M; t_T]} M_z^{[m_R, m_T; m_M]}$$

Coordination symbols are added to the symbols of the chemical elements as trailing superscripts and placed between square brackets. Symbols before a semicolon refer to the heteronuclear coordination (r_T, r_M for R ; t_R, t_M for T and m_R, m_T for M) and those after it to the homonuclear coordination (r_R, t_T and m_M). The form of a coordination polyhedron can be further indicated by a small letter, as for example p for a prism, where the number (or the sum of the numbers) before the letter indicates the number of the vertices.

The simplified crystal-chemical formulae of the particular ternary Ni aluminides of interest here, taking into account the known coordination polyhedra of the R ($= Y$ or U) and Ni atoms, can be written as



Based on the simple fact that the number of bonds extended from all atoms i to the atoms ii must be equal to the number of bonds extended from all atoms ii to the atoms i it is possible to calculate the average values of t_R and t_{Al} and to rewrite the crystal-chemical formulae as



From this result it is possible to calculate that the ratio of the number of Ni-centred trigonal prisms of composition R_2Al_4 to the total number of Ni-centred trigonal prisms (compositions R_2Al_4 and Al_6) is

equal to x/y ; that means the ratio of the number of R_2Al_4 prisms to the number of Al_6 prisms (normalized to one formula unit) is 1:0 in YNiAl₄, 4:1 in U₄Ni₅Al₁₈ and 4:2 in Y₄Ni₆Al₂₃.

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Structure of a Thallium(I) Transition-Metal Carbonyl Salt Tl[Fe(CO)₃(NO)]

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Abstract. Thallium tricarbonylnitrosoiron, $M_r = 374.25$, cubic, $P2_13$, $a = 8.853(1) \text{ \AA}$, $V = 693.8 \text{ \AA}^3$, $Z = 4$, $D_x = 3.582 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 254.8 \text{ cm}^{-1}$, $F(000) = 656$, $T = 240 \text{ K}$, $R = 0.0197$ for 420 unique observed reflections. Discrete Tl^+ cations are well separated by $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ anions

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in a distorted NaCl-like structure; the shortest distance between cations is 5.621 (1) Å, and there are no direct Tl...Tl covalent bonding interactions. Nitrosyl and carbonyl groups in the approximately tetrahedral anion are all essentially linear.

Introduction. There has recently been resurgence of interest in the structural chemistry of thallium(I), not least because of the short Tl...Tl interactions which are found in some compounds; an excellent review of this area, together with an insight into the nature of the thallium–thallium bond, has appeared (Janiack & Hoffmann, 1990). Many examples of thallium atoms bonded to the transition-metal centres in organometallic fragments or clusters are also known (Compton, Errington & Norman, 1990), but an important class of compound of this type has received little recent attention. These complexes can be represented by the general formula Tl[ML_n], where ML_n is a monoanionic, 18-electron, transition-metal carbonyl group and the thallium is univalent. Several compounds of this type have been reported, in which $[ML_n]^-$ is $[M(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$ ($M = \text{Cr, Mo, W}$), $[\text{Mn}(\text{CO})_5]^-$, $[\text{Co}(\text{CO})_3(L)]^-$ $\{L = \text{CO, PR}_3, \text{P}(\text{OR})_3\}$, $[\text{V}(\text{CO})_6]^-$, $[\text{Fe}(\text{CO})_3(L)(R')]^-$ $\{L = \text{CO, R}' = \text{CH}_2\text{CN, CPh, CN, SnPh}_3; L = \text{PR}_3, \text{P}(\text{OR})_3, \text{R}' = \text{SnPh}_3\}$ and $[\text{Fe}(\text{CO})_2(L)(\text{NO})]^-$ $\{L = \text{PR}_3, \text{P}(\text{OR})_3\}$ (Burlitch & Theyson, 1974; Pedersen & Robinson, 1975). The reports concentrated on the synthesis of the compounds and, in particular, on their solution-state properties with regard to the presence or absence of a thallium–transition-metal bond. There is infrared spectroscopic evidence for the presence of a Tl– M bond in some cases, although separated ions or close-ion pairs involving Tl–OC– M linkages are clearly present in certain solvents, but very few data have been presented for the solid state, the only crystal structure determination of which we are aware being for Tl[$\text{Co}(\text{CO})_4$] (1) (Schussler, Robinson & Edgell, 1974; Klüfers, 1983). Here we report the structure of the related complex Tl[$\text{Fe}(\text{CO})_3(\text{NO})$] (2), which we synthesized as part of our own studies on thallium(I)–transition-metal complexes.

Experimental. Synthesis of (2): a solution of TlNO_3 (0.226 g, 0.848 mmol) in deoxygenated distilled water (10 cm^3) was added to solid $[\text{Me}_4\text{N}][\text{Fe}(\text{CO})_3(\text{NO})]$ (0.207 g, 0.848 mmol) and the resulting dark yellow-brown solution was stirred for 2 h. During this time a grey precipitate formed (presumably thallium metal, since it dissolved in methanol with gas evolution). After removal of the water from the reaction solution by vacuum, a dark red-brown residue was obtained, which was extracted in toluene (20 cm^3) and filtered through celite. The filtrate was concentrated to about 5 cm^3 and hexane (20 cm^3) was layered over it. Dark red block-like crystals were

obtained by solvent diffusion at 243 K over a period of four days. This preparation is a modification of that given by Pedersen & Robinson (1975).

Crystallography: a crystal of size 0.23 × 0.31 × 0.31 mm, sealed in a Lindemann capillary, was examined on a Stoe–Siemens diffractometer, equipped with an Oxford Cryostream cooler (Cosier & Glazer, 1986). Unit-cell parameters were refined from 2 θ values of 32 reflections (20–25°) measured at $\pm \omega$. Data collection was performed in the ω/θ -scan mode with on-line profile fitting (Clegg, 1981), to a maximum 2 θ of 50°; the maximum value of all three indices was ten, and several equivalent sets of data were collected, including complete sets of Friedel opposites. No significant variation was observed in the intensities of three standard reflections; semi-empirical absorption corrections were applied, based on sets of equivalent reflections measured at a range of azimuthal angles: transmission factors ranged from 0.002 to 0.013. From a total of 3914 measured reflections, 420 unique data were obtained, all of which were considered to be observed, with $F > 4\sigma_c(F)$ (σ_c from counting statistics only); $R_{\text{int}} = 0.057$. The observed $m\bar{3}$ Laue symmetry and systematic absences $h00$ for odd values of h uniquely determine the space group $P2_13$.

Atoms were located from Patterson and difference syntheses, and subjected to blocked-cascade least-squares refinement on F , weighting $w^{-1} = \sigma^2(F) = \sigma_c^2(F) - 14 + 61G - 21G^2 + 35H - 20H^2 - 88GH$ [$G = F_o/F_{\text{max}}$, $H = \sin\theta/\sin\theta_{\text{max}}$ (Wang & Robertson, 1985)], and with anisotropic thermal parameters for all atoms. An isotropic extinction parameter x refined to $9(2) \times 10^{-7}$, whereby $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$. The absolute structure was confirmed by refinement of $\eta = 1.12(7)$ (Rogers, 1981). At convergence, $R = 0.0197$, $wR = 0.0214$, $S = 0.97$ for 32 parameters; mean $\Delta/\sigma = 0.002$, maximum $\Delta/\sigma = 0.013$. A final difference synthesis showed no features outside the range -1.21 to $+0.57 \text{ e \AA}^{-3}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149); *SHELXTL* (Sheldrick, 1985) and local computer programs were used. Atomic coordinates and anisotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The structure consists of Tl^+ cations and $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ anions. Each cation is surrounded by six anions and each anion has six cation neighbours; the structure can be considered as derived from that of NaCl; the packing of the ions is shown

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54529 (3 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>			
Tl	656.8 (3)	<i>x</i>	<i>x</i>			
Fe	5577.6 (12)	<i>x</i>	<i>x</i>			
N	6659 (7)	<i>x</i>	<i>x</i>			
O(1)	7450 (6)	<i>x</i>	<i>x</i>			
C	5939 (8)	3578 (9)	5633 (10)			
O(2)	6177 (8)	2300 (6)	5631 (7)			
	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Tl	60.9 (2)	<i>U</i> ₁₁	<i>U</i> ₁₁	-1.1 (1)	<i>U</i> ₂₃	<i>U</i> ₂₃
Fe	55.6 (3)	<i>U</i> ₁₁	<i>U</i> ₁₁	-1.6 (5)	<i>U</i> ₂₃	<i>U</i> ₂₃
N	61 (2)	<i>U</i> ₁₁	<i>U</i> ₁₁	2 (3)	<i>U</i> ₂₃	<i>U</i> ₂₃
O(1)	91 (3)	<i>U</i> ₁₁	<i>U</i> ₁₁	-21 (3)	<i>U</i> ₂₃	<i>U</i> ₂₃
C	68 (5)	65 (3)	64 (4)	-2 (4)	6 (4)	-6 (3)
O(2)	97 (4)	61 (3)	84 (3)	-1 (3)	10 (4)	-1 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Fe—N	1.659 (11)	Fe—C	1.800 (8)
N—O(1)	1.212 (14)	C—O(2)	1.150 (9)
N—Fe—C	116.7 (3)	C—Fe—C	101.4 (3)
Fe—N—O(1)	180.0	Fe—C—O(2)	178.3 (8)

Symmetry operator: (i) *z*, *x*, *y*.

in Fig. 1. A similar description has been given for the structure of Tl[Co(CO)₄] (1) (Schussler, Robinson & Edgell, 1974). However, although these two thallium compounds have the same space group and a very similar cell parameter, they are not isostructural. We presumed at first that they were, and took the published atomic coordinates for (1) as initial parameters for (2), only to find to our surprise that refinement was unsuccessful. In a similar way, the final coordinates obtained for (2) could not be refined to fit the data for (1) (available as supplementary material of the original publication), and inspection of the two sets of data showed them to be quite different. The two structures have a similar packing arrangement in gross terms, and both have all the ions on threefold rotation axes, but the arrangement relative to the 2₁ screw axes (and hence the cell origin) is different and inequivalent.

The nitrosyl group of the anion in (2) lies along a threefold rotation axis, so it is precisely linear. The three symmetry-equivalent carbonyl groups are also linear within experimental error, as was found in the case of (1) by a redetermination of the structure at a lower temperature (Klüfers, 1983). The Fe—N bond is shorter than Fe—C, while N—O is longer than C—O, as is usual in nitrosyls and carbonyls. Angular distortions from ideal tetrahedral values at iron are such as to compress the three carbonyl groups slightly together, away from the single nitrosyl group, the three C—Fe—C angles being about 8° below, and the three C—Fe—N angles about 7° above the regular 109.5° tetrahedral angle. Precise C₃ (3) and essential C_{3v} (3*m*) symmetry is maintained

for the [Fe(CO)₃(NO)]⁻ anion in this solid-state structure.

The 6:6 distorted NaCl-like packing of the ions precludes any Tl...Tl covalent interactions, the shortest distances between cations being 5.621 (1) Å. The closest atoms to Tl⁺ ions are oxygen atoms of the anions and also the corresponding nitrogen and carbon atoms. The six Tl⁺ cations closest to each anion are three interacting with one carbonyl each [O...Tl 3.081 (6) Å, C—O...Tl 137.6 (6)°] and three which each contact the NO and two CO groups [nitrosyl O...Tl 3.591 (4), N...Tl 3.262 (1) Å; carbonyl O...Tl 3.780 (6) and 4.241 (6) Å, C...Tl 3.363 (9) and 3.712 (8) Å]. This arrangement produces shortest Tl...Fe contacts of 3.509 (1) Å, with the other carbonyl group almost directly opposite Tl [Tl...Fe—C 171.6 (8)°]. These cation-anion interactions are shown in Fig. 2. Since the complex anions are much

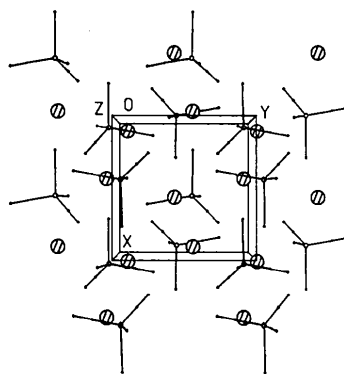
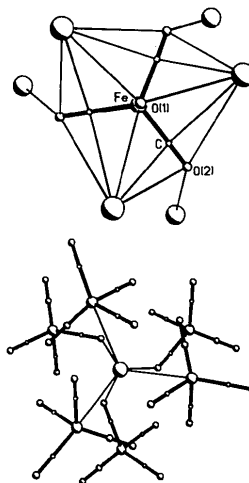
Fig. 1. Packing of the ions in (2). Tl⁺ cations are shown as large shaded circles.

Fig. 2. Environments of the anions (top: view along the nitrosyl group towards iron, the largest atoms are thallium) and cations (bottom: view along a body diagonal, interactions are shown only to the carbonyl oxygen atoms of three anions at 3.081 Å and to iron of three anions at 3.509 Å).

larger than the monatomic cations, there are also short intermolecular contacts for the nitrosyl and carbonyl groups, the shortest O...O distance being 3.075 (10) Å. These simply represent close packing of the ions, rather than any significant specific interactions. Iron atoms are all at least 5.677 (2) Å apart. In summary, the structure of (2) [as well as that of (1)] is ionic, with no Ti—Fe or Ti—Ti covalent bonding.

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Structure of $\text{Pb}_2\text{MnFe}_2\text{F}_{12}\cdot 3\text{H}_2\text{O}$

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Abstract. Diiron dilead manganese dodecafluoride trihydrate, $M_r = 863.06$, hexagonal, $P\bar{6}2m$, $a = 9.320$ (1), $c = 3.9618$ (5) Å, $V = 298.0$ (1) Å³, $Z = 1$, $D_x = 4.81$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 31.95$ mm⁻¹, $F(000) = 337$, room temperature, $R = 0.032$ for 845 unique reflections, crystal growth by hydrothermal synthesis in HF solution. The structure presents three chains of MF_6 octahedra ($M = \text{Fe}^{3+}$, Mn^{2+} statistically distributed on the same site) sharing *trans* corners along [001] and connected by *cis* corners to form a triple infinite isolated chain of formula $[\text{M}_3\text{F}_{12}]_n^{4n-}$. The structure is related to the CsCrF_4 type; however, the Cs-atom site is occupied by the water molecule and the Pb atom occupies a trigonal prism of F atoms tricapped by the water molecules.

Introduction. Investigations of $\text{PbF}_2\text{--FeF}_3\text{--MF}_2\text{--HF}_{\text{aq}}$ systems ($M = \text{Mn, Zn, Cu}$) by hydrothermal synthesis reveal to date two new low-dimensional structure types. One of them, having the $\text{Pb}_8\text{MF}_2\text{F}_{24}$ formulation, is characterized by a structure containing infinite isolated $[\text{MFe}_2\text{F}_{14}]_n^{6n-}$ chains of corner-sharing octahedra inserted into a fluorite-like matrix (Le Bail & Mercier, 1991). The second structure type is that of $\text{Pb}_2\text{MnFe}_2\text{F}_{12}\cdot 3\text{H}_2\text{O}$, whose determination is presented here; it is built up from completely different condensed chains.

Experimental. A few hexagonal prismatic light brown single crystals of $\text{Pb}_2\text{MnFe}_2\text{F}_{12}\cdot 3\text{H}_2\text{O}$ were grown by hydrothermal synthesis in 1 M HF solution following a procedure described by Plet, Fourquet, Courbion, Leblanc & De Pape (1979). Platinum tube, volume 4.41 cm³, filling rate 60%, 1.25×10^{-3} mol of nominal composition $\text{Pb}_2\text{MnFe}_2\text{F}_{12}$ in 2.5 cm³ 1 M HF, heating rate 300 K h⁻¹, final temperature $T_f = 573$ K, stage to reach T_f 3 d, cooling rate 30 K h⁻¹, initial pressure 100 MPa, P at $T_f = 160$ MPa. Phases also present: $\text{Pb}_8\text{MnFe}_2\text{F}_{24}$ and at least one other, currently being investigated.

Data collected on a Siemens AED-2 four-circle diffractometer. Prismatic crystal $0.13 \times 0.10 \times 0.12$ mm. ω - 2θ step-scan mode in 36 steps of $\Delta\omega = 0.035^\circ$. Time per step $t_{\text{min}} = 1$ s, $t_{\text{max}} = 4$ s. Lattice constants based on 30 reflections at $2\theta \approx 30^\circ$. Absorption correction by the Gauss method $A_{\text{max}} = 0.17$, $A_{\text{min}} = 0.06$. Intensity measurement of two independent sets to $2\theta_{\text{max}} = 90^\circ$ within the range $-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $0 \leq l \leq 8$. Standard reflections $\bar{4}21$, $\bar{2}1\bar{2}$, $\bar{2}4\bar{1}$, intensity variation 1.0%. 2557 reflections measured, 845 independent reflections used for refinements [$|F| > 6\sigma(|F|)$], $R_{\text{av}} = 0.040$. Structure solved by Patterson method. F magnitudes used in least-squares refinements, 26 parameters refined, $\Delta/\sigma_{\text{max}} = 0.001$, secondary extinction $x = 0.0059$ (5), scattering factors for Pb^{2+} , Mn^{2+} ,