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Structure of Thallium Nitroprusside

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Abstract. $Tl_2[Fe(CN)_5(NO)]$, monoclinic, *Cc*, $a = 13{\cdot}349\,(15)$, $b = 12{\cdot}520\,(9)$, $c = 6{\cdot}779\,(5)$ Å, $\beta = 66{\cdot}180\,(1)°$, $Z = 4$, $D_c = 4{\cdot}003$ Mg m^{-3}, $\mu = 32{\cdot}802$ mm^{-1} (Mo $K\alpha$), $F(000) = 1063$. The structure was solved by the heavy-atom method and refined, with constraints in the first stages, to an R of 0·067 for 738 unique reflections. The structure is tightly packed with a shortest Tl—Tl distance of 3·480 (2) Å. The nitrosyl groups of neighbouring nitroprusside ions form a staggered stack along the *c* axis with a mean separation of 4·8 Å; directions of consecutive groups form an angle of approximately 55°.

Introduction. The determination of the structure of thallium nitroprusside was undertaken as part of a series of chemical, spectroscopic, TGA–DTA and structural studies of nitroprusside compounds (Lanfranconi, Alvarez & Castellano, 1973; Alvarez, Aymonino, Baran, Gentil, Lanfranconi & Varetti, 1976; Castellano, Piro & Rivero, 1977*a*,*b*; Rivero *et al.*, 1978; Castellano, Piro, Podjarny, Rivero, Aymonino, Lesk & Varetti, 1978; Punte, Rigotti, Rivero, Podjarny & Castellano, 1980).

Crystals were obtained by slow evaporation from an aqueous solution. A crystal of irregular shape (maximum and minimum linear dimensions of about 0·4 and 0·3 mm respectively) was mounted on an Enraf–Nonius CAD-4 diffractometer. Intensities were measured by the θ–2θ scan technique at a rate of 1·33–20·0° min^{-1}, determined by a fast pre-scan of 20° min^{-1}. 738 unique reflections above background (3σ) were collected using graphite-monochromated Mo $K\alpha$ radiation in the range $1° < 2\theta < 48°$. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The systematic absences (hkl: $h + k = 2n$; $h0l$: $l = 2n$) suggested space group *Cc* or *C*2/*c*. Statistical intensity tests and the cell content indicated the space group *Cc*.

The positions of the two Tl and Fe atoms were obtained from a Patterson map. A difference map

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phased on these atoms did not show any physically meaningful atomic peaks. Three cycles of refinement of the positional parameters of the heavy atoms were then carried out, bringing the R factor down from 34·6% to 26·6%. Three more cycles with isotropic thermal parameters lowered the R factor further to 11·62%. In spite of the few atoms located up to this stage, full-matrix least squares was used because these atoms made up approximately 70% of the scattering matter.

An unweighted difference map phased only on the refined parameters of both Tl atoms showed most of the atoms of the nitroprusside ion. In subsequent maps all the atoms were located with the exception of one N of a CN group. This atom, near to a Tl atom and probably masked by the anisotropic ripple of this heavy atom, was approximately positioned from the known stereochemistry of the nitroprusside ion.

A block-matrix least-squares refinement of the structure was then carried out. Bonds within the nitroprusside ion that had been constrained, and the positional parameters of both Tl atoms which had been kept fixed during initial blocked cycles of refinement, were gradually freed. A full least-squares refinement with isotropic temperature factors for the atoms in the nitroprusside ion converged to an $R\,[=\sum(|F_o|-|F_c|)/\sum|F_o|]$ of 0·067. The final atomic positional and thermal parameters are given in Table 1;* bond distances and angles for the nitroprusside ion are shown in Table 2. The numbering scheme used and a perspective view of the two asymmetric units in the cell are shown in Fig. 1.

Table 1. *Positional parameters* ($\times 10^4$ *for* Tl *and* Fe; $\times 10^3$ *for* C, N *and* O) *and isotropic temperature factors* ($\times 10^3$ *for* Tl *and* Fe; $\times 10^2$ *for* C, N *and* O), *with e.s.d.'s in parentheses*

	x	y	z	U_{iso} (Å^2)
Tl(1)	0	320	0	*
Tl(2)	3613 (2)	1176 (2)	5306 (5)	*
Fe	1509 (5)	2972 (5)	2946 (10)	122 (13)
C(1)	68 (3)	403 (3)	478 (6)	6 (7)
C(2)	225 (4)	159 (4)	173 (8)	26 (11)
N(3)	189 (3)	349 (3)	49 (6)	12 (7)
C(4)	120 (3)	226 (3)	565 (6)	5 (8)
C(5)	281 (4)	348 (4)	337 (8)	28 (12)
C(6)	18 (4)	229 (4)	295 (7)	17 (9)
N(1)	15 (4)	464 (3)	598 (7)	24 (9)
N(2)	254 (4)	78 (4)	94 (7)	35 (11)
O(1)	216 (3)	390 (3)	−110 (6)	30 (9)
N(4)	108 (4)	184 (4)	730 (7)	34 (11)
N(5)	352 (4)	388 (3)	377 (7)	31 (10)
N(6)	−59 (3)	200 (3)	296 (7)	25 (9)

* The anisotropic thermal parameters for these atoms are:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	378 (12)	265 (11)	187 (9)	4 (8)	−120 (8)	13 (9)
Tl(2)	235 (11)	262 (12)	568 (15)	−20 (10)	−186 (10)	46 (9).

Table 2. *Bond distances* (Å) *and angles* (°) *for the nitroprusside ion with e.s.d.'s in parentheses*

Fe–C(1)	1·84 (4)	C(1)–N(1)	1·14 (6)
Fe–C(2)	1·96 (5)	C(2)–N(2)	1·14 (7)
Fe–C(4)	1·92 (4)	C(4)–N(4)	1·19 (6)
Fe–C(5)	1·97 (5)	C(5)–N(5)	1·20 (7)
Fe–C(6)	1·97 (4)	C(6)–N(6)	1·08 (6)
Fe–N(3)	1·67 (4)	N(3)–O(1)	1·12 (5)
C(1)–Fe–C(2)	164·0 (1·9)	C(6)–Fe–C(2)	85·2 (1·9)
C(1)–Fe–N(3)	104·6 (1·7)	C(6)–Fe–N(3)	94·7 (1·7)
C(2)–Fe–N(3)	91·3 (1·9)	C(6)–Fe–C(4)	87·1 (1·7)
C(1)–Fe–C(4)	81·3 (1·6)	C(6)–Fe–C(5)	169·8 (2·0)
C(2)–Fe–C(4)	82·9 (1·8)	N(1)–C(1)–Fe	176·6 (3·6)
N(3)–Fe–C(4)	173·8 (1·6)	N(2)–C(2)–Fe	169·4 (4·6)
C(5)–Fe–C(1)	89·7 (1·9)	O(1)–N(3)–Fe	175·2 (3·4)
C(5)–Fe–C(2)	91·3 (2·1)	N(4)–C(4)–Fe	175·4 (3·6)
C(5)–Fe–N(3)	95·1 (2·0)	N(5)–C(5)–Fe	172·4 (4·4)
C(5)–Fe–C(4)	82·9 (1·9)	N(6)–C(6)–Fe	173·3 (10·5)
C(6)–Fe–C(1)	91·0 (1·7)		

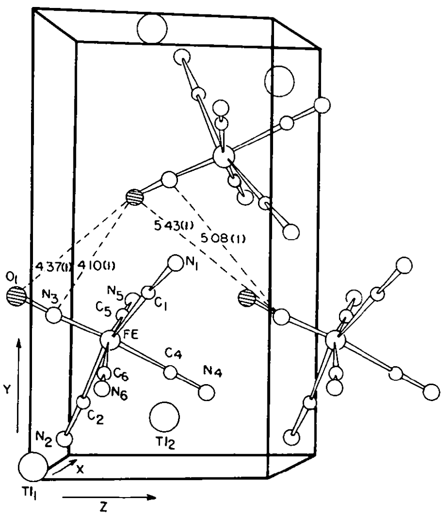

Fig. 1. Perspective view of the unit-cell contents, showing some intermolecular contacts (Å).

In all scattering-factor calculations, form-factor tables computed from numerical Hartree–Fock wavefunctions were used (Cromer & Mann, 1968) corrected for relativistic anomalous-scattering effects (Cromer & Liberman, 1970).

Discussion. Because of the presence of the c glide plane, the nitrosyl groups form a staggered stack along the c axis, as can be seen in Fig. 1. Neighbouring nitrosyl groups make an angle of approximately 55°.

This result differs from determinations on alkaline-earth nitroprussides (Manoharan & Hamilton, 1963;

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35080 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Minimum distances between heavy atoms* (Å) *with e.s.d.'s in parentheses*

Tl(1^{i})–Tl(1^{ii})	3·480 (2)
Tl(1^{i})–Tl(2^{iii})	4·706 (7)
Tl(2^{i})–Tl(2^{ii})	4·492 (5)
Tl(1^{i})–Fe^{i}	4·730 (3)
Tl(2^{i})–Fe^{i}	4·370 (4)

Symmetry code

(i)	x,y,z
(ii)	$x,\bar{y},0{\cdot}5+z$
(iii)	$z,y,1-z$

Lanfranconi *et al.*, 1973; Castellano *et al.*, 1977*a*; Punte *et al.*, 1980) where it has been found that the nitrosyl groups are piled up antiparallel to one another. It also differs from the determinations on $[As(C_6H_5)_4]_2$-$[Fe(CN)_5(NO)]$ and $[P(C_6H_5)_4]_2[Fe(CN)_5(NO)]$ (Castellano *et al.*, 1977*b*) where the nitrosyl groups neither are oriented in a specific direction nor are close to each other.

The nitroprusside ion has a very distorted octahedral configuration with the metal atom displaced from the equatorial cyanide plane towards the nitrosyl group. This result is in agreement with all other determinations on nitroprusside salts (Manoharan & Hamilton, 1963; Lanfranconi *et al.*, 1973; Castellano *et al.*, 1977*a*,*b*; Punte *et al.*, 1980). As was pointed out in those papers, the short Fe–N(3) distance indicates that the NO group is strongly bonded to the Fe atom, in agreement with the interpretation of Ballhausen & Gray (1963), Mössbauer-effect measurements (Danon, 1963) and MO calculations (Manoharan & Gray, 1965).

The structure is very tightly packed, with rather short distances between the heavy atoms, Table 3. This packing is probably the cause of the large distortion of the expected octahedral coordination around the Tl ions.

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