Thallium Dicyanoaurate(I), Tl[Au(CN)₂], and Cesium Dicyanoaurate(I), Cs[Au(CN)₂]

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Abstract. Tl[Au(CN)₂]: $M_r = 453 \cdot 373$, orthorhombic, *Pbcn*, $a = 7 \cdot 092$ (2), $b = 30 \cdot 429$ (7), $c = 9 \cdot 140$ (5) Å, $V = 1972 \cdot 4$ (2·2) Å³, $Z = 16$, $D_m = 6 \cdot 00$ (13), $D_x = 6 \cdot 105$ Mg m⁻³, neutrons, $\lambda = 1 \cdot 0405$ (9) Å, $\mu = 0 \cdot 048$ mm⁻¹, $T = 298$ K, $F(000) = 777 \cdot 0$ fm, $R = 0 \cdot 038$ for 587 observed reflections. Cs[Au(CN)₂]: $M_r = 381 \cdot 908$, orthorhombic, *Pbcn*, $a = 7 \cdot 42$ (1), $b = 32 \cdot 67$ (1), $c = 9 \cdot 369$ (3) Å, $V = 2271 \cdot 2$ (5·3) Å³, $Z = 16$, $D_x = 4 \cdot 46$ (1) Mg m⁻³, Mo $K\bar{\alpha}$, $\lambda = 0 \cdot 7107$ Å, $\mu = 31 \cdot 96$ mm⁻¹, $T = 298$ K, cell constants determined only. There are three crystallographically inequivalent [Au(CN)₂]⁻ ions in the unit cell of Tl[Au(CN)₂], two of which are linear, parallel to **b** and related by pseudo-translation; the third is approximately linear, parallel to the *ab* plane and inclined by 51° to **b**. The [Au(CN)₂]⁻ units form a two-dimensional network of relatively short Au···Au distances [Tl salt: 3·037 (4), 3·068 (4), 3·560 (1) Å]. Cs[Au(CN)₂] was found to be isostructural to Tl[Au(CN)₂] from precession photographs.

Introduction. The [Au(CN)₂]⁻ ion in solution shows a charge-transfer absorption at >40 000 cm⁻¹. Crystalline M[Au(CN)₂] [M = K, Rb, Cs, Tl, (*n*-C₄H₉)₄N] salts show the corresponding absorption shifted to lower energies by up to 20 000 cm⁻¹ (Tl: 20 300 cm⁻¹, Cs: 16 300 cm⁻¹) (Mason, 1976; Blom, 1983). This behavior is similar to that observed for [Pt(CN)₄]²⁻ and its crystalline salts. In the latter case the variation in absorption energies has been explained in terms of linear arrays of [Pt(CN)₄]²⁻ ions in which some ions are related by other than translational symmetry, the Pt···Pt distances (3·1–3·7 Å) and the resulting Davydov splitting (Day, 1975). In an attempt to understand the spectroscopic properties of the M[Au(CN)₂] salts we have undertaken a series of crystal structure analyses.

Experimental. Tl[Au(CN)₂] was prepared by precipitation from aqueous solutions of Tl₂SO₄ and K[Au(CN)₂]. Single crystals of a size suitable for neutron diffraction experiments were grown by a temperature-gradient technique (Arend, 1982). Density determined by measuring the loss of weight in water. Cell parameters from 22 reflections with $11 \cdot 5 \le \theta \le 15 \cdot 1°$. CAD-4 diffractometer, Mo $K\bar{\alpha}$ radiation.

Interpretation of X-ray diffraction data entails several problems since absorption of X-rays is high [μ(Mo $K\bar{\alpha}$) = 61·19 mm⁻¹]. Therefore, 1302 neutron diffraction intensities (including 210 intensities absent in *Pbcn*) were collected from a crystal 1·14 × 2·14 × 3·08 mm (along **a**, **b**, **c** respectively) on the four-circle diffractometer of the Institut für Reaktortechnik at the reactor Saphir (Würenlingen, Switzerland). The angle ψ was chosen such that the reciprocal vector (*hkl*) corresponding to the reflection being measured and its two nearest neighbors, *i.e.* the vectors (*h,k*±1,*l*) ($b = 30 \cdot 429$ Å), were in the equatorial plane. The detector window was carefully adjusted to receive the full width of the diffracted beam only. This procedure maximizes the resolution between neighboring reflections for pure ω scans; it also ensures maximum resolution for the ω:*gθ*-scan technique used here (*g* between 1·5 and 2·0; Pantazatos & Werner, 1973; Werner, 1971). Data were collected in the range (sinθ/λ) < 0·525 Å⁻¹, 0 < H < 6, 0 < K < 29, 0 < L < 8. Intensities of standard reflections varied statistically by <0·95% ($\bar{8}$02), 1·08% (060), 1·13% (004) during the six-months period of data collection. Data reduction, Lorentz and absorption corrections (Tichý, 1973); transmission factors 0·922 to 0·964. 1092 reflections allowed in *Pbcn*, 743 observed [$F > 3\sigma(F)$], 587 unique ($R_{int} = 0 \cdot 0094$). Phase determination by direct methods [*SHELX*76 (Sheldrick, 1976) and *MULTAN*80 (Main, Fiske, Hull,

Lessinger, Germain, Declercq & Woolfson, 1980)] failed, probably because of pseudosymmetry (see below). A substructure was determined from a Patterson map and the full structure inferred by trial and error. Refinement on F's. The model was partially anisotropic (75 parameters) with equal vibrational parameters for those C, N, Tl and Au atoms that are related by pseudotranslation (see below). All Au(CN)$_2$ groups were constrained to have the same Au—C and C≡N distances ($\sigma = 0.002$); their refined values were 1.971 and 1.147 Å respectively. Refinement of independent vibrational and positional parameters for all atoms resulted in statistically significant improvement of R values, but introduced high correlation coefficients between parameters of atoms related by pseudotranslation. For the restrained and constrained model final $R = 0.038$, $wR = 0.037$. Final weights $w = 4.5152/\{[\sigma(F)]^2 + 0.0001F^2\}$. In the last least-squares cycle $(\Delta/\sigma)_{max} = 0.043$. No feature in the difference Fourier map calculated after the final refinement exceeded $+0.45$ and -0.49 fm Å^{-3} ($+1.8$, -2.0% of the max. peak height of 24.7 fm Å^{-3} in an F_o Fourier map). Secondary extinction accounted for by using the extinction factor included in the program SHELX76 [$F' = F(1-0.0001pF^2/\sin\theta)$, $p = 0.219$ (9)]. Neutron scattering lengths (fm) 9.39 (N), 8.9 (Tl), 7.6 (Au) and 6.64 (C) (International Tables for X-ray Crystallography, 1974).

Cs[Au(CN)$_2$] was prepared from an aqueous solution of K[Au(CN)$_2$] by ion exchanging K$^+$ for H$^+$ and subsequently neutralizing with CsOH. Cell parameters were refined from 20 reflections in the θ range 11.0 to 14.5° measured on a CAD-4 diffractometer with Mo $K\bar{\alpha}$ radiation.

Discussion. Tl[Au(CN)$_2$]. The refined atomic positions and thermal parameters are given in Table 1*. Fig. 1 shows an ORTEP (Johnson, 1976) drawing of the contents of the unit cell. Interatomic distances and angles are given in Table 2, and the coordination of Tl$^+$ is shown in Figs. 2(a) and 2(b).

The crystal structure of Tl[Au(CN)$_2$] shows pseudosymmetry. All atoms except for Au(3), N(31) and N(32) occupy positions that are within ±0.3 Å of the values they would have in a structure with cell constants $a' = a$, $b' = b/2$, $c' = c$ and the (nonstandard) space group Imcb. On going from Pbcn to Imcb, two different sets of Wyckoff positions (orbits) $4(c)$ $(0,y,\frac{1}{4})$ occupied by Au(1) and Au(2), respectively, in Pbcn merge into one orbit in Imcb, namely $4(a')$ $(\frac{1}{4},0,0)$. Similarly four different orbits $4(c)$ occupied by C(11), C(12), C(21), C(22) in Pbcn merge into one orbit in

Imcb, $8(f')$ $(\frac{1}{4},y',0)$. The same applies to N(11), N(12), N(21), N(22). The two different orbits $8(d)$ (x,y,z) occupied by Tl(1) and Tl(2), respectively, in Pbcn merge into orbit $8(j')$ $(0,y',z')$. The same argument applies to C(31) and C(32). The I-centered substructure includes 73% of the scattering power in the unit cell.

The Au(3) atoms occupy a single orbit $8(d)$ in Pbcn. In neighboring cells along the b' axis in Imcb the atoms Au(3) alternately occupy one or the other half of the Wyckoff position $8(g')$, namely $(\frac{1}{4}, 0, z'; \frac{1}{4}, 0, -z'; \frac{3}{4}, \frac{1}{2}, \frac{1}{2} + z'; \frac{3}{4}, \frac{1}{2}, \frac{1}{2} - z')$ or $(\frac{3}{4}, 1, z'; \frac{3}{4}, 1, -z'; \frac{1}{4}, -\frac{1}{2}, \frac{1}{2} + z'; \frac{1}{4}, -\frac{1}{2}, \frac{1}{2} - z')$. The atoms N(31) and N(32) occupy different orbits $8(d)$ in Pbcn, but the same orbit $16(k')$ (x', y', z') in Imcb. Only half of the positions of this orbit are filled. The distribution of N(31) and N(32) at these positions is analogous to that of Au(3). This distribution of Au(3), N(31) and N(32) is responsible for the most intense superstructure reflections $F(hkl)$ with $k = 2n + 1$ (in Pbcn).

The pseudosymmetry described here is different from and more complex than that arising from so-called non-characteristic and extraordinary orbits (Wondratschek, 1976; Engel, 1983). In both of these cases choice of special coordinate values for one particular orbit leads to a system of points whose symmetry is higher than the symmetry generating the system of points in the first place. In our case two or more different orbits in the lower-symmetry space group merge to form a single orbit in the higher-symmetry space group.

The [Au(CN)$_2$]$^-$ ions are approximately linear, the Au—C and C—N bond lengths are in agreement with those found in the K[Au(CN)$_2$] structure (Rosenzweig & Cromer, 1959). Au···Au distances of 3.037 (4) [Au(1)—Au(3)] and 3.068 (4) Å [Au(3)—Au(3)] are found between three [Au(CN)$_2$]$^-$ ions almost equally spaced in the c direction. The observed Au(1)—Au(2) distance of 3.560 (1) Å is slightly longer than $a/2$ (3.546 Å) because of a slight difference in the y coordinates of Au(1) and Au(2).

Coordination around Tl$^+$ is highly irregular and slightly different for the two Tl$^+$ ions. Three N ligands are situated at ca 2.85 Å from Tl with Tl—N—C angles between 120 and 155°, one or two N ligands between 3.0 and 3.2 Å from Tl with Tl—N—C angles ranging from 97 to 115°, and a number of CN$^-$ ions are at >3.4 Å in side-on position to the Tl$^+$. The environment of Tl$^+$ is completed by an Au—C group at ca 3.45 Å (Fig. 2).

Cs[Au(CN)$_2$]. This salt is isostructural to the Tl salt. An Au(1)—Au(2) distance of 3.71 (1) Å is predicted if it is assumed to equal $a/2$. Au(1)—Au(3) and Au(3)—Au(3) distances are 3.12 (1) Å assuming that the Au atoms are equally spaced along the c axis. With positional coordinates taken from the Tl salt and cell constants from the Cs salt, the resulting distances are 3.72 (1) [Au(1)—Au(2)], 3.11 (1) [Au(1)—Au(3)] and

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39520 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3·14 (1) Å [Au(3)—Au(3)]. In any case, the Au···Au distances are notably longer than in the Tl salt.

The implications of the crystal structures described here on the luminescence properties are discussed elsewhere (Blom, 1983).

Table 1. *Fractional coordinates and equivalent iso-tropic temperature factors* (Å²) (*e.s.d.'s in units of least significant digit in parentheses*)

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

|	x	y	z	U_{eq}
Tl(1)	0·7802 (3)	0·2828 (1)	0·4138 (7)	0·041 (4)
Tl(2)	0·2242 (3)	0·4692 (1)	0·4179 (7)	0·041
Au(1)	0·0	0·1210 (1)	0·25	0·034 (7)
C(11)	0·0	0·1858 (1)	0·25	0·035 (3)
N(11)	0·0	0·2235 (1)	0·25	0·048 (15)
C(12)	0·0	0·0562 (1)	0·25	0·035 (3)
N(12)	0·0	0·0185 (1)	0·25	0·049 (16)
Au(2)	0·5	0·1316 (1)	0·25	0·034
C(21)	0·5	0·1963 (1)	0·25	0·035
N(21)	0·5	0·2340 (1)	0·25	0·049
C(22)	0·5	0·0668 (1)	0·25	0·035
N(22)	0·5	0·0292 (1)	0·25	0·048
Au(3)	0·5020 (4)	0·3763 (1)	0·4178 (2)	0·032 (7)
C(31)	0·2857 (5)	0·3356 (1)	0·4117 (5)	0·040 (8)
N(31)	0·1640 (4)	0·3110 (1)	0·4022 (4)	0·066 (11)
C(32)	0·7183 (5)	0·4170 (1)	0·4132 (5)	0·040
N(32)	0·8381 (4)	0·4422 (1)	0·4045 (4)	0·066
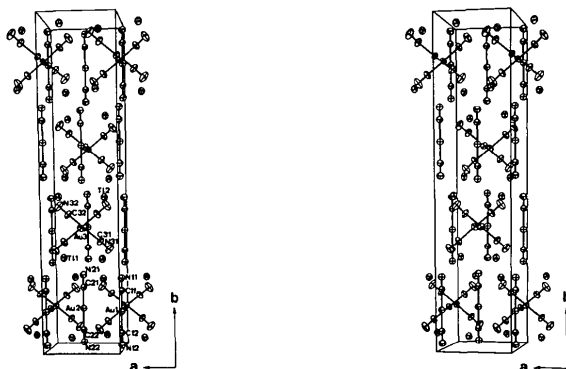
Fig. 1. A stereoscopic view of the structure (*ORTEP*; Johnson, 1976). Thermal ellipsoids are drawn to include 50% probability.
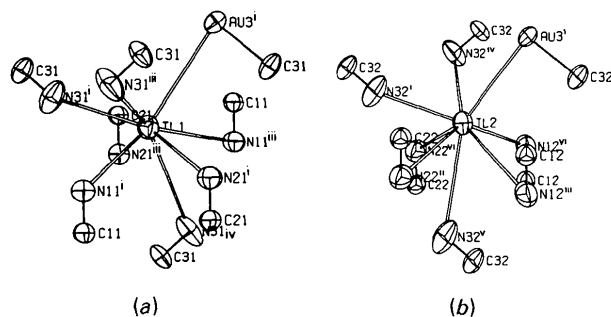

(a)   (b)

Fig. 2. (a) Coordination of Tl(1). (b) Coordination of Tl(2).

Table 2. *Interatomic distances* (Å) *and angles* (°) (*e.s.d.'s in units of least significant digit in parentheses*)

[Au(CN)₂]⁻ group

Au(1)—C(11)	1·970 (2)	C(11)—N(11)	1·148 (2)
Au(1)—C(12)	1·971 (2)	C(12)—N(12)	1·148 (2)
Au(2)—C(21)	1·971 (2)	C(21)—N(21)	1·145 (2)
Au(2)—C(22)	1·970 (2)	C(22)—N(22)	1·146 (2)
Au(3)—C(31)	1·972 (2)	C(31)—N(31)	1·145 (2)
Au(3)—C(32)	1·971 (2)	C(32)—N(32)	1·147 (2)

C(31)—Au(3)—C(32)	177·1 (2)	Au(3)—C(31)—N(31)	176·6 (4)
		Au(3)—C(32)—N(32)	175·8 (4)

All other C—Au—C and Au—C—N angles are 180° by symmetry.

Au···Au distances

Au(1)—Au(2ⁱ)	3·560 (1)	Au(1)—Au(3ⁱⁱ)	3·037 (4)
		Au(3)—Au(3ⁱᵛ)	3·068 (4)

Coordination around Tl⁺*

Tl(1)—N(11ⁱ)	2·815 (4)	C(11)—N(11)—Tl(1)	129·8 (1)
Tl(1)—N(11ⁱⁱⁱ)	3·664 (4)	C(11)—N(11)—Tl(1)	87·0 (2)
Tl(1)—N(21ⁱ)	2·897 (4)	C(21)—N(21)—Tl(1)	120·8 (1)
Tl(1)—N(21ⁱⁱⁱ)	3·483 (4)	C(21)—N(21)—Tl(1)	81·6 (1)
Tl(1)—N(31ⁱ)	2·857 (4)	C(31)—N(31)—Tl(1)	155·9 (3)
Tl(1)—N(31ⁱᵛ)	3·040 (4)	C(31)—N(31)—Tl(1)	99·1 (3)
Tl(1)—N(31ⁱⁱⁱ)	3·414 (4)	C(31)—N(31)—Tl(1)	109·2 (2)
Tl(1)—Au(3ⁱ)	3·463 (4)	C(31)—Au(3)—Tl(1)	85·8 (2)
Tl(2)—N(12ᵛⁱ)	2·904 (4)	C(12)—N(12)—Tl(2)	121·1 (1)
Tl(2)—N(12ⁱⁱⁱ)	3·631 (4)	C(12)—N(12)—Tl(2)	84·1 (2)
Tl(2)—N(22ᵛⁱ)	2·866 (4)	C(22)—N(22)—Tl(2)	129·5 (1)
Tl(2)—N(22ⁱⁱ)	3·427 (4)	C(22)—N(22)—Tl(2)	89·2 (2)
Tl(2)—N(32ⁱ)	2·861 (4)	C(32)—N(32)—Tl(2)	154·0 (3)
Tl(2)—N(32ⁱᵛ)	3·091 (4)	C(32)—N(32)—Tl(2)	97·9 (3)
Tl(2)—N(32ᵛ)	3·179 (4)	C(32)—N(32)—Tl(2)	115·4 (3)
Tl(2)—Au(3ⁱ)	3·446 (4)	C(32)—Au(3)—Tl(2)	86·0 (2)

* Superscripts indicate symmetry operations applied to N or Au positional parameters as given in Table 1: (i) x, y, z; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iv) $-x, +y, \frac{1}{2} - z$; (v) $-x, -y, -z$; (vi) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$. Translations by a full unit cell are omitted. Symmetry operations are not given for the atoms defining angles. They are the same as for the corresponding distances next to them.

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