Dicesium Sodium Dicyanoaurate(I), Cs₂Na[Au(CN)₂]₃. Crystal-Chemical Relationship to Potassium Dicyanoaurate(I) and -argentate(I)

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Abstract. $M_r = 1035 \cdot 804$, hexagonal, $P6_3/mmc$, $a = 7 \cdot 0679$ (7), $c = 18 \cdot 2566$ (56) Å, $V = 789 \cdot 8$ (4) Å³, $Z = 2$, $D_x = 4 \cdot 381$ Mg m⁻³, Mo $K\bar{\alpha}$, $\lambda = 0 \cdot 7107$ Å, $\mu = 32 \cdot 24$ mm⁻¹, $T = 298$ K, $F(000) = 872$, $R = 0 \cdot 032$, 328 observed reflections. The six [Au(CN)₂]⁻ units in the cell are parallel to **c** and form a two-dimensional network of relatively short Au···Au distances [3·448 (1), 3·620 (1) Å].

Introduction. This is the second in a series of crystal structure analyses undertaken with the aim of understanding the luminescence properties of [Au(CN)₂]⁻ salts. For part one see Blom, Ludi, Bürgi & Tichý (1984).

Experimental. Attempts to crystallize Cs[Au(CN)₂] yielded two types of crystals. One type shows visible luminescence upon irradiation with UV light, the other does not. The former was found to be Cs[Au(CN)₂], isomorphous to Tl[Au(CN)₂] whose structure is described in Blom *et al.* (1984). Here we describe the structure of the second class of crystals, a byproduct of the synthesis of Cs[Au(CN)₂]. Hexagonal unit cell from precession photographs, space group $P6_3/mmc$. Crystal structure determination, elemental and X-ray fluorescence analyses showed the composition Cs₂Na[Au(CN)₂]₃ and $Z = 2$. Na introduced as an impurity (1·13%) in CsOH used for the synthesis of Cs[Au(CN)₂] (Blom, 1983). Cell parameters from 20 reflections with $16 \cdot 6 \le \theta \le 20 \cdot 4°$. Hexagonal prismatic crystal form (0·1056 mm between prism faces, 0·3131 mm long). CAD-4 diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation, ω-scan technique, all reflections measured in 'needle mode' to minimize absorption effects, variable scan rate 0·42 to 5° min⁻¹. 2018 reflections, of which 352 unique ($R_{int} = 0 \cdot 0152$), $-8 < H < 7$, $-2 < K < 8$, $-5 < L < 23$, $\sin\theta/\lambda < 0 \cdot 6378$ Å⁻¹; of these, 328 had $F > 6\sigma(F)$ and were used in subsequent calculations. Intensities of standard reflections varied statistically, average F_o after absorption correction 1234 (2) (205), 1216 (3) ($\bar{2}$05), 1215 (3) (0$\bar{2}$5), 1242 (3) (02$\bar{5}$) and 344 (2) (0,0,22). Lorentz–polarization and absorption corrections applied (transmission factors 0·0599 to 0·0936; Engel, 1977, 1978). Au and Cs positions from a Patterson map; C, N, and Na from successive difference Fourier maps. Refinement on F's of anisotropic Au, Cs and Na and isotropic C and N (17 parameters) led to $R = 0 \cdot 032$, $wR = 0 \cdot 043$. Refinement of anisotropic temperature factors for C and N resulted in statistically significant improvement of R values, introduced correlations between vibrational parameters on the same atom, but did not provide additional chemical information. A difference Fourier map shows a peak at 0·5, 0·33, 0·25 of height 3·2 e Å⁻³. It sits at the center of a cavity formed by a barrel of six parallel [Au(CN)₂]⁻ units and two Cs⁺ ions (Fig. 1). The distances from the center to Au are 3·534 (1) Å, to Cs⁺ 3·461 (1) Å. The peak appears only when extinction corrections are applied and is weak compared to the peaks obtained for C and N in an F_o Fourier map (11·4 and 16·1 e Å⁻³, respectively). Nevertheless it is tempting to interpret the feature in that large a cavity in terms of an occupant. Unfortunately, water is ruled out by the absence of a corresponding sharp O–H stretching band in the IR spectrum and by elemental analysis; but then, what else could it be? At present we cannot offer a conclusive interpretation of this feature in the electron density difference map. Residual electron density $< +1 \cdot 41$ and $> -0 \cdot 81$ e Å⁻³ elsewhere and is probably due to inadequacies of the absorption correction ($\mu = 32 \cdot 24$ mm⁻¹!). Weighting scheme $w = 7 \cdot 4652/\{[\sigma(F)]^2 + 0 \cdot 0001F^2\}$. In the last least-squares cycle $(\Delta/\sigma)_{max} = 0 \cdot 005$. Extinction correction included in the program *SHELX*76 [Sheldrick (1976); $F' = F(1 - 0 \cdot 0001pF^2/\sin\theta)$, $p = 0 \cdot 0015$]. Complex scattering factors for neutral atoms [Au, Cs, Na from *International Tables for X-ray Crystallography* (1974); C, N from Cromer & Mann (1968), Cromer & Liberman (1970)]. Values of the mass absorption coefficient from *International Tables* (1968). Fourier syntheses, least-squares and geometry calculations performed with the program *SHELX*76 (Sheldrick, 1976).

Discussion. The refined atomic positions and thermal parameters are given in Table 1.* Fig. 1 shows a stereoscopic picture (Johnson, 1976) of the unit-cell contents. Interatomic distances and angles are given in Table 2, and coordination around Cs^+ and Na^+ ions is shown in Figs. 2(a) and 2(b), respectively.

The crystals used for diffraction experiments were investigated with polarized light. They show a structure of concentric zones whose zone axis is parallel to **c**. The refractive indices in the *ab* plane show a slight $(n_\beta - n_\alpha < 0.001)$ but clearly visible difference indicating an orthorhombic distortion. Since Na^+ was present only in small amounts in the solution phase and since $Cs_2Na[Au(CN)_2]_3$ crystallized before $Cs[Au(CN)_2]$, the concentration of Na^+ steadily decreased, thus explaining the zonal structure of the $Cs_2Na[Au(CN)_2]_3$ crystals. The reason for the orthorhombic distortion is not well understood. Differences of up to 6% in F between reflections equivalent in $P6_3/mmc$, but inequivalent in the corresponding orthorhombic space group $Cmcm$, exist but are not significant if compared to the possible errors in the absorption correction (up to 15%). Of the reflections present, but treated as systematically absent in $P6_3/mmc$, some have actually been observed, but only $\overline{489}$ shows $F > 6\sigma(F)$. Thus, from the diffraction data a slight orthorhombic distortion can be neither proved nor excluded. The structure was refined in $P6_3/mmc$ because this model fits the data satisfactorily with the minimum number of parameters.

The $[Au(CN)_2]^-$ ions are approximately linear. The Au—C and C—N bond lengths are in agreement with those found in $K[Au(CN)_2]$ and $Tl[Au(CN)_2]$ (Rosenzweig & Cromer, 1959; Blom *et al.*, 1984). The environment of Cs^+ (site symmetry $3m$) consists of three CN groups coordinated approximately end-on with Cs—N bond distances of 3.31 (1) Å and six CN groups coordinated side-on with Cs—N bond lengths of 3.55 (1) Å. Side-on coordination is only achieved at larger Cs—N distances. Analogous observations have been made for Tl^+ coordination in $Tl[Au(CN)_2]$ (Blom *et al.*, 1984). Na^+ has site symmetry $\overline{3}m$ and is coordinated to six CN groups with Na—N distances of 2.50 Å and C—N—Na angles of 128.6 (6)°.

The architecture of the $Cs_2Na[Au(CN)_2]_3$ structure shows similarities to those of $K[Au(CN)_2]$ and $K[Ag(CN)_2]$ (Hoard, 1933). In all three structures the Au atoms are arranged in layers perpendicular to the *c* axis {$K[Au(CN)_2]$: hexagonal setting}; the layers can be described as closest packed with one out of four atoms missing. Every Au atom has four nearest neighbors in a rectangular environment (Fig. 3; for clarity, only two of the three short Au···Au contacts

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39521 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic temperature factors* (Å^2) *(e.s.d.'s in units of least significant digit in parentheses)*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
Na	0.0	0.0	0.5	0.043 (3)
Cs	0.3333	0.6667	0.5604 (1)	0.0508 (4)
Au	0.1707 (1)	0.3414 (1)	0.25	0.0485 (4)
C	0.1683 (6)	0.337 (1)	0.3564 (7)	0.037 (2)
N	0.1646 (7)	0.329 (1)	0.4189 (9)	0.068 (4)

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

Au(CN)$_2$|$^-$ group			
Au—C	1.94 (1)	C—Au—C	178.3 (3)
C—N	1.14 (2)	N—C—Au	178.6 (6)

Coordination around Cs^+*

Cs—N^{i,ii,iii}	3.31 (1)	C—N—Cs	139.1 (6)
Cs—N^{iv,v,v,vi,vi}	3.55 (1)	C—N—Cs	96.1 (6)

Coordination around Na^+*

Na—N^{vii,viii,ix,x,xi,xii}	2.50 (1)	C—N—Na	128.6 (6)
		N^{viii}—Na—N^x	88.5 (5)

* Superscripts indicate symmetry operations applied to N positional parameters as given in Table 1: (i) x, y, z; (ii) $-y, x - y, z$; (iii) $y - x, -x, z$; (iv) $-x, -y, -z$; (v) $y, y - x, -z$; (vi) $x - y, x, -z$; (vii) $-x, -y, \frac{1}{2} + z$; (viii) $x, y, \frac{1}{2} - z$; (ix) $y, y - x, \frac{1}{2} + z$; (x) $-y, x - y, \frac{1}{2} - z$; (xi) $x - y, x, \frac{1}{2} + z$; (xii) $y - x, -x, \frac{1}{2} - z$; translations by a full unit cell are omitted.
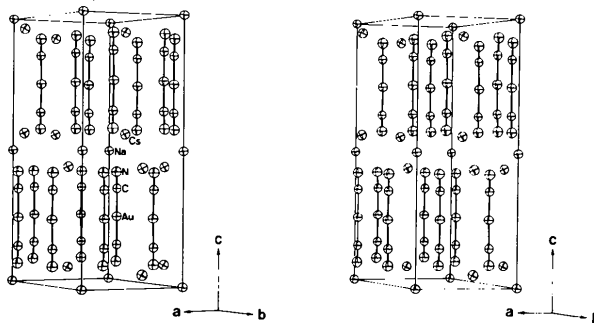

Fig. 1. A stereoscopic view of the structure (*ORTEP*; Johnson, 1976). Thermal ellipsoids are drawn to include 50% probability.
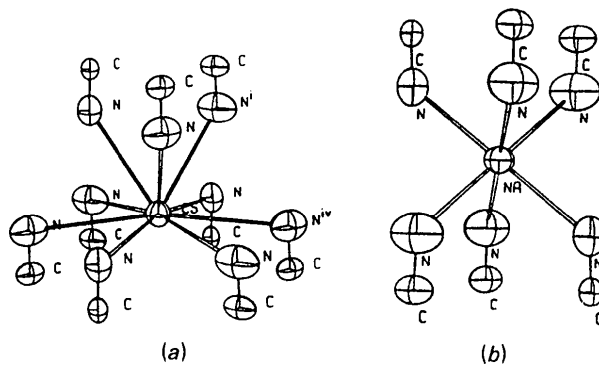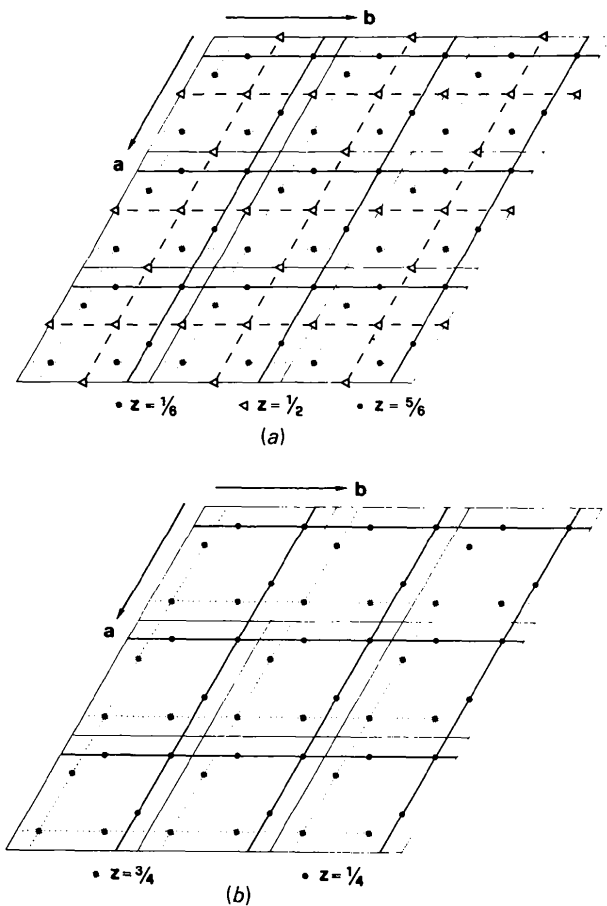

(a)   (b)

Fig. 2. (a) Coordination of Cs^+. (b) Coordination of Na^+.

Fig. 3. Layers of Au atoms in (a) K[Au(CN)₂], K[Ag(CN)₂] and (b) Cs₂Na[Au(CN)₂].

within a layer are indicated). In K[Au(CN)₂], all Au···Au nearest-neighbor distances within layers (3·64 Å) are equivalent by symmetry; in K[Ag(CN)₂] the Ag···Ag distances are the same to within experimental accuracy [3·69 (2) Å]. In Cs₂Na[Au-(CN)₂]₃, two nearest-neighbor Au···Au distances are observed [3·448 (1), 3·620 (1) Å]. The structures of K[Au(CN)₂] and K[Ag(CN)₂] show three successive

layers of anions whose stacking may be described as ...ABC...; the structure of Cs₂Na[Au(CN)₂]₃ shows only two layers stacked as ...AC.... Because of the different stacking sequences, the ratio of the c axes of the Au compounds is expected to be ~1·5; it is observed to be 1·44. The discrepancy may be understood in terms of the orientation of the linear [Au(CN)₂]⁻ ions relative to the stacking axis. In K[Au(CN)₂], they are tilted 20° to this axis. This reduces the thickness of the [Au(CN)₂]⁻ layers compared to Cs₂Na[Au(CN)₂]₃ where the [Au(CN)₂]⁻ ions are parallel to the stacking axis. There are two different types of environment for the K⁺ ions in K[Au(CN)₂], one similar to that of Na⁺ and one similar to that of Cs⁺, respectively, in Cs₂Na[Au(CN)₂]₃. The tilting of the [Au(CN)₂]⁻ ions in K[Au(CN)₂] distorts the environment observed for Cs⁺ in Cs₂Na[Au(CN)₂]₃ towards octahedral coordination, in agreement with the coordinative preferences of K⁺. For the same reasons Ag(CN)₂ groups in K[Ag(CN)₂] are tilted by ~27° with respect to the stacking axis.

The implications of the crystal structure for the luminescence properties are discussed elsewhere (Blom, 1983).

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Structure of the Tin Antimony Sulphide Sn₆Sb₁₀S₂₁

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Abstract. $M_r = 2603·0$, monoclinic, $C2/m$, $a = 44·995$ (5), $b = 3·9023$ (5), $c = 20·613$ (3) Å, $\beta = 96·21$ (1)°, $V = 3598·1$ (5) Å³, $Z = 4$, $D_x = 4·80$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 124·5$ cm⁻¹, $F(000) = 4584$, $T = 293$ K. Final $R = 0·0704$ for 1573 observed data. The structure (previously reported as