Anomalous Temperature Dependence of the Structure of TlAu(CN)₂ Investigated by High-Resolution Neutron Powder Diffraction

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By means of high-resolution neutron powder diffraction (sample-limited resolution $\delta d/d \geq 10^{-3}$, d = lattice spacing) the temperature dependence of the orthorhombic structure of the pseudosymmetric layer compound TlAu(CN)₂ was investigated in the range from 5 to 300 K in connection with optical measurements. No phase transition occurs, but similar to KAu(CN)₂, the longest lattice parameter b increases anomalously with decreasing temperature, from 30.460 Å at 300 K to 30.851 Å at 5 K. When the [Au(CN)₂]⁻ ions are constrained to be linear, the b-lattice parameter increase is found to be due to the reduction of the angle between the [Au(3)(CN)₂]⁻ ion and the b-axis, from 50.7° at 300 K to 47.6° at 5 K. Apart from these essential changes the results confirm the structure model of Blom et al., corresponding to space group *Pbcn* as derived previously from a single-crystal neutron diffraction measurement at room temperature. Short interatomic distances Au–Au approaching 3 Å at 5 K indicate significant Au–Au overlap, causing (with Au–Tl covalent overlap) the particular yellow color of TlAu(CN)₂.

Introduction

The colorless salts of cyanoaurate(I), $M^+[Au(CN)_2]^-$ (M = K, Rb, Cs), show characteristic luminescence at remarkably low energies.[1] In these compounds Au(I) has a d¹⁰ electron configuration. A special case is the thallium(I) salt, whose unique bright yellow color cannot be attributed to a single ion property but is indicative of a considerable metal–metal interaction.[2] In the course of a study related to the electronic structure of MAu(CN)₂ compounds, an investigation of the temperature dependence of the luminescence of the Tl(I) salt was carried out. An earlier single-crystal neutron diffraction structure analysis of TlAu(CN)₂ established at room temperature[3] an orthorhombic, pseudosymmetric crystal structure model corresponding to space group *Pbcn*. There are three crystallographic inequivalent [Au(CN)₂]⁻ ions in the unit cell. Two of these N–C–Au–C–N ions are linear and are oriented parallel to the b-axis, and the third ion is approximately linear, almost parallel to the (a,b)-plane and inclined 51° to [010] at room temperature [maximum angle deviation from $180° \approx -4°$ for Au(3)–C(32)–N(32)]. Layers of [Au(CN)₂]⁻ ions alternate with layers of Tl⁺ ions along the b-axis. In the former layers, relatively short Au–Au distances of the order of 3 Å exist at room temperature, which suggests considerable metal–metal interaction.

As information concerning phase transitions and structure variations as a function of temperature is crucial for a thorough discussion of the optical properties, neutron diffraction investigations were started on a powder sample of TlAu(CN)₂ in the temperature range from 5 to 300 K at Würenlingen and continued later with higher resolution at ILL, Grenoble. Compared to X-rays, neutron scattering offers the essential advantages of high sensitivity to light atoms such as C and N as well as little absorption. Powder diffraction enables us to follow in a straightforward manner the structural changes as a function of parameters such as temperature. By means of the present investigations, it could be shown that an anomalous b-lattice parameter increase exists in TlAu(CN)₂ with decreasing temperature to 5 K; this increase is mainly related to a reorientation of the [Au(3)(CN)₂]⁻ ion. The investigation is also of interest with respect to the state of high-resolution powder neutron diffraction using constant-wavelength machines. In particular, it was found to be necessary to use chemical constraints in the present (rather complicated) case with a chemical unit cell implying 17 different atom sites and a b-lattice parameter of the order of 30 Å. Already in the single-crystal study,[3] all Au–C and C–N distances were constrained to equal values. Only preliminary results of the present study were published in abstract form.[4]

Experiment and Data Analysis

The polycrystalline sample of TlAu(CN)₂ was prepared as described in ref 3. For the neutron diffraction measurements, the powder was enclosed under a helium gas atmosphere in a cylindrical vanadium container of 8-mm diameter and approximately 5-cm height.

The high-resolution multidetector neutron powder diffractometer DMC[5] situated at the Saphir reactor of the Paul Scherrer Institut, Würenlingen, Switzerland was used for the first measurements at 293 and 7 K. The lower scattering angle range $2\theta = 3°$ to 83° was scanned with a step $\delta(2\theta) = 0.10°$ to search for structural phase transitions as a function of temperature. The neutron wavelength $\lambda = 1.7100$ Å was used, as obtained from a Ge(3,1,1) monochromator (collimations 10′/ 20′/≥12′, resolution $\delta d/d \geq 4 \times 10^{-3}$, d = lattice spacing). The DMC data were corrected for absorption according to the measured transmission (product of linear absorption coefficient and radius μr = 0.215).

Because of the large b-lattice parameter and the considerable number of structural parameters of TlAu(CN)₂, further neutron diffraction investigations were performed on the high-resolution neutron powder diffractometer D2B[6] at ILL, Grenoble, France, in the temperature range from 5 to 300 K ($\lambda = 1.5946$ Å, Ge(5,3,3) monochromator, collimations 5′/-/5′, scattering angle step $\delta(2\theta) = 0.025°$, 2θ range up to ≈162°, sample-limited resolution $\delta d/d \geq 10^{-3}$). The measured profile intensities (about 6500) comprise approximately 2000 inequivalent reflections h,k,l.

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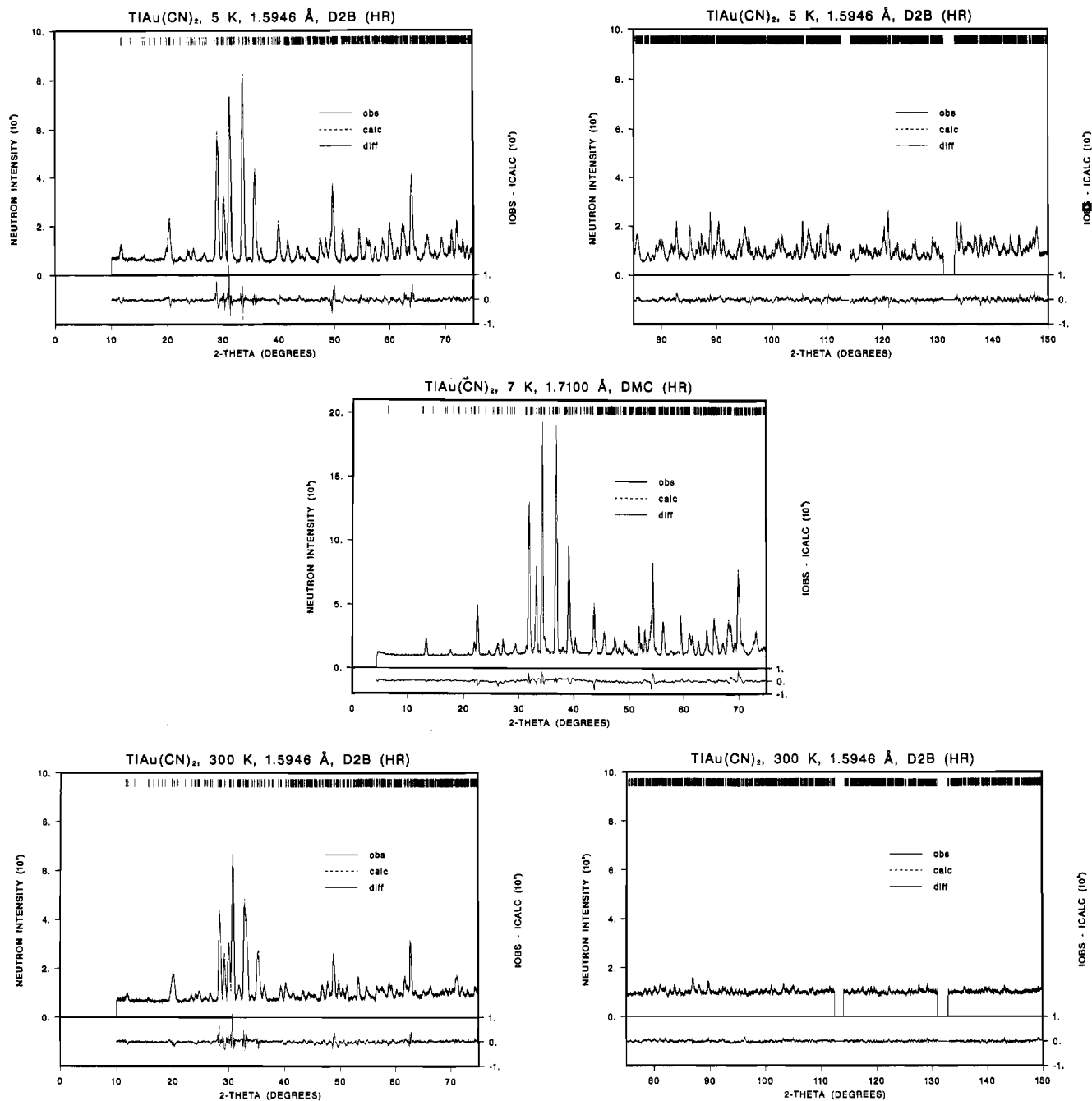
Figure 1. Observed, calculated, and difference neutron diffraction patterns of TlAu(CN)₂: (a) at 5 K, D2B/ILL high-resolution measurement with $\delta(2\theta) = 0.025°$; (b) at 7 K, DMC/Würenlingen, $\delta(2\theta) = 0.10°$, based on structural parameters according to measurement (a) and (c) at 300 K, D2B/ILL high-resolution measurement with $\delta(2\theta) = 0.025°$. A comparison of the 5 and 7 K diagrams shows that the deviations between calculated (based on Gaussian peak shape with low-angle asymmetry) and observed profile intensities for 5 K at low scattering angles are mainly caused by monochromator problems of D2B in connection with vertical divergence effects. (An essentially better monochromator based on a new concept is in progress.) Excluded regions are caused by additional impurity peaks, which could not be uniquely identified (e.g. AuCN and possibly one Al cryostat peak at high scattering angles).

Absorption corrections were neglected in case of the D2B data, as their effect (mainly on the temperature factors) is small in the present case.

For such a large pseudosymmetric structure, unconstrained refinements (cf. also Table 4) yielded some chemically unreasonable interatomic distances and bond angles, especially at high temperature, so that the neutron diffraction patterns were finally analyzed with chemical constraints (cf. ref 3) using the MORGUE program[7] including automatic background fitting. Nuclear neutron scattering amplitudes published by Sears[8] were used. In order to limit the number of structural parameters to a minimum, we used isotropic temperature factors, which should be a fair approximation at least at low temperatures. At room temperature

the refinement based on the positional parameters determined previously by single-crystal neutron diffraction[3] yielded the same goodness of fit value χ^2 as a refinement with identical, strictly linear [Au(CN)₂]⁻ ions according to the bond distances Au–C = 1.97 Å and C–N = 1.15 Å. Therefore we also used these values to constrain the low-temperature refinements. Unconstrained refinements resulted in the same values, within error limits of approximately two standard deviations. Refined "molecular" parameters were the molecule center positions and Euler angles. In addition we varied the positional parameters of Tl(1) and Tl(2).

Neutron Diffraction Results

Illustrative neutron diffraction patterns of TlAu(CN)₂ are shown in Figure 1. Below scattering angles of approximately

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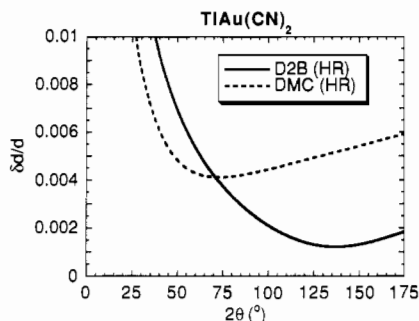
Figure 2. Measured high-resolution functions $\delta d/d$ of diffractometers D2B/ILL and DMC/Würenlingen for TlAu(CN)$_2$ at low temperature where particle size broadening can be seen. d = lattice spacing.

70°, the resolution of DMC is better than that of D2B, as may be seen more explicitly from Figure 2 displaying the measured resolution functions. On the other hand, the resolution of D2B is considerably higher at large scattering angles, but for this material was apparently sample limited, as the instrument configuration implies $\delta d/d \approx 5 \times 10^{-4}$.[6] A comparison of the 5 and 300 K neutron diffraction patterns shows remarkable changes, in particular at low scattering angles, which at first glance might suggest a structural phase transition. However the differences turned out to be mainly caused by the anomalous temperature dependence of the lattice parameter b, which is shown in Figure 3. The temperature dependences of the relevant "molecular" parameters and isotropic temperature factors are given in Tables 1 and 2. Positional parameters refined at 5 K are summarized in Table 3. Finally, shortest interatomic distances based on Tables 1–3 are given in Table 4. Figure 4 illustrates the 5 K crystal structure of TlAu(CN)$_2$, based on the structural parameters shown in Table 3.

Optical Results

The room-temperature luminescence spectrum of TlAu(CN)$_2$ consists of a strong peak at 488 nm (20 500 cm^{-1}) when the sample is excited at 337 nm.[2] Lowering the temperature from 300 to 5 K results in a decrease in the TlAu(CN)$_2$ luminescence energy

Table 1. Data for Temperature T, Refinement Type, Number of Parameters Varied n_{par}, Agreement Values R_{wp} and R_{exp} Concerning Weighted Profile Intensities and As Expected from Counting Statistics, Respectively, Goodness of Fit $\chi^2 = (R_{wp}/R_{exp})^2$, tilt Angle ϕ, and Euler Angle θ of [Au(3)(CN)$_2$]$^-$ for TlAu(CN)$_2$ (B = Temperature Factor)

T (K)	refinement	n_{par}	R_{wp}	R_{exp}	χ^2	ϕ (deg)	θ (deg)
300	xyz^3	22	5.55	3.45	2.58		
300	linear	35	5.54	3.45	2.58	50.74(6)	91.6(3)
293	$xyz,^3 B$(300 K)	15	6.74	2.73	6.13		
180	linear	35	6.17	3.97	2.41	49.39(5)	90.5(2)
80	linear	35	6.50	3.44	3.56	48.32(4)	90.2(1)
7	xyz, B(5 K)	15	5.85	2.35	6.22		
5	linear	35	6.98	3.44	4.11	47.62(3)	90.1(1)
5	xyz^3	22	9.42	3.48	7.33		
5	only B constr	53	6.28	3.44	3.34		

Table 2. Temperature Dependences of Isotropic Temperature Factors B (Å^2) of TlAu(CN)$_2$ Determined by "Linear" Refinements[a]

	T (K)			
	5	80	180	300
B[Au(1)]	0.38(4)	0.77(5)	1.53(7)	2.98(11)
B[C(11)]	0.51(4)	0.75(4)	1.76(6)	3.17(9)
B[N(11)]	1.06(3)	1.60(4)	2.79(5)	4.41(8)
B[Au(3)]	0.65(6)	1.13(5)	2.02(8)	3.00(11)
B[C(31)]	0.69(5)	1.06(5)	2.40(8)	3.99(13)
B[N(31)]	1.26(4)	1.98(5)	3.72(8)	6.35(15)
B[Tl(1)]	0.51(4)	1.06(4)	1.95(4)	3.26(8)

[a] Temperature factor constraints are similar to those of ref 3: B[Au(2)] = B[Au(1)], B[C(22)] = B[C(21)] = B[C(12)] = B[C(11)], B[C(32)] = B[C(31)], B[N(22)] = B[N(21)] = B[N(12)] = B[N(11)], B[N(32)] = B[N(31)], and B[Tl(2)] = B[Tl(1)].

of 1130 cm^{-1}. This can be compared to KAu(CN)$_2$, where lowering the temperature from 300 to 78 K results in a decrease in luminescence energy of 1100 cm^{-1}.[1]

Discussion and Conclusions

In the temperature range from 300 to 5 K, no phase transition is observed for TlAu(CN)$_2$, but an anomalous, approximately linear increase of the largest lattice parameter b occurs with
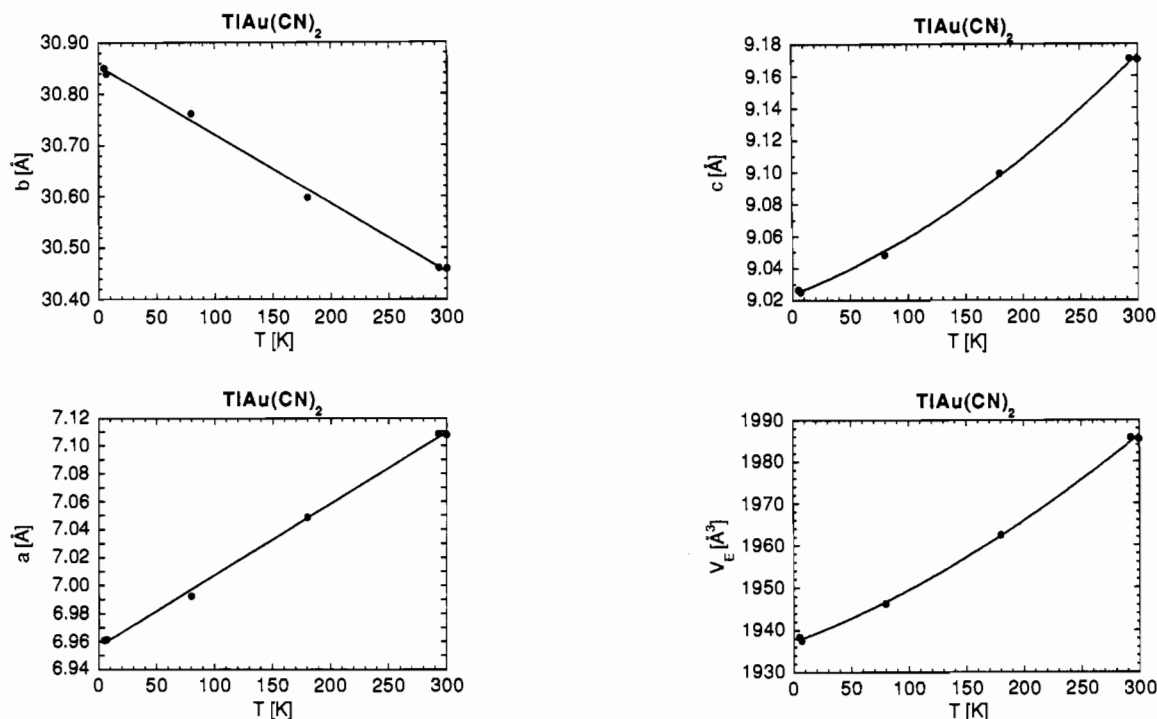
Figure 3. Temperature dependences of lattice parameters a–c and of unit cell volume V_E of TlAu(CN)$_2$. Note the anomalous temperature variation of lattice parameter b. The lines correspond to linear/polynomial (of degree 2) fits for $(a,b)/(c$ and $V_E)$, respectively.

Table 3. Positional Parameters Obtained from "Linear" and "Only *B*-Restricted" Refinements (Lower Values) at 5 K

atom	x	y	z
Au(1)	0.0000	0.1208(1)	0.2500
		0.1208(3)	
N(11)	0.0000	0.2220	0.2500
		0.2227(2)	
C(11)	0.0000	0.1847	0.2500
		0.1855(3)	
C(12)	0.0000	0.0570	0.2500
		0.0553(3)	
N(12)	0.0000	0.0197	0.2500
		0.0193(2)	
Au(2)	0.5000	0.1304(1)	0.2500
		0.1309(2)	
N(21)	0.5000	0.2316	0.2500
		0.2326(2)	
C(21)	0.5000	0.1943	0.2500
		0.1931(3)	
C(22)	0.5000	0.0666	0.2500
		0.0663(3)	
N(22)	0.5000	0.0293	0.2500
		0.0296(2)	
Au(3)	0.5028(4)	0.3762(1)	0.4102(2)
	0.5031(8)	0.3764(2)	0.4170(4)
N(32)	0.8338	0.4444	0.4099
	0.8319(6)	0.4457(1)	0.4028(7)
C(32)	0.7118	0.4193	0.4100
	0.7171(9)	0.4180(2)	0.4155(10)
C(31)	0.2937	0.3332	0.4104
	0.2901(9)	0.3331(2)	0.4091(11)
N(31)	0.1717	0.3081	0.4106
	0.1683(6)	0.3079(1)	0.4053(7)
Tl(1)	0.7768(7)	0.2815(2)	0.4191(11)
	0.7777(6)	0.2812(2)	0.4166(9)
Tl(2)	0.2307(6)	0.4705(2)	0.4117(11)
	0.2298(6)	0.4707(2)	0.4162(9)

Table 4. Selected Interatomic Distances in TlAu(CN)$_2$ as Functions of Temperature, As Obtained from "Linear" Refinements[a]

bond (Å)	T (K)				
	5	80	180	300	≈300 ³
Au(1)–C(11)*	1.970/1.994(11)[b]	1.970	1.970	1.970	1.970(2)
Au(1)–C(12)*	1.970/2.020(11)	1.970	1.970	1.970	1.971(2)
Au(2)–C(21)*	1.970/1.919(10)	1.970	1.970	1.970	1.971(2)
Au(2)–C(22)*	1.970/1.992(10)	1.970	1.970	1.970	1.970(2)
Au(3)–C(31)*	1.970/1.997(9)	1.970	1.970	1.970	1.972(2)
Au(3)–C(32)*	1.970/1.966(9)	1.970	1.970	1.970	1.971(2)
Au(2)–Au(1)	3.493/3.4943(9)	3.510	3.537	3.569	3.560(1)
Au(3)–Au(1)	3.069/3.008(3)	3.079	3.087	3.116	3.037(4)
Au(3)–Au(3)	2.893/3.014(7)	2.893	2.928	2.942	3.068(4)
Au(3)–Tl(1)	3.492/3.505(8)	3.469	3.411	3.388	3.463(4)
Au(3)–Tl(2)	3.471/3.477(8)	3.457	3.476	3.465	3.446(4)
N(11)–C(11)*	1.150/1.148(10)	1.150	1.150	1.150	1.148(2)
N(12)–C(12)*	1.150/1.111(10)	1.150	1.150	1.150	1.148(2)
N(21)–C(21)*	1.150/1.220(10)	1.150	1.150	1.150	1.145(2)
N(22)–C(22)*	1.150/1.132(10)	1.150	1.150	1.150	1.146(2)
N(31)–C(31)*	1.150/1.151(8)	1.150	1.150	1.150	1.145(2)
N(32)–C(32)*	1.150/1.177(8)	1.150	1.150	1.150	1.147(2)
Tl(1)–N(11)	2.849/2.825(8)	2.856	2.861	2.964	2.815(4)
Tl(1)–N(31)	2.869/2.844(6)	2.847	2.823	2.816	2.857(4)
Tl(2)–N(12)	2.819/2.814(7)	2.832	2.866	2.828	2.904(4)
Tl(2)–N(22)	2.828/2.827(8)	2.841	2.840	2.793	2.866(4)
Tl(2)–N(32)	2.878/2.876(6)	2.894	2.897	2.909	2.861(4)

[a] An asterisk indicates a constrained value. [b] These second values at 5 K correspond to a refinement with "only *B* constraints".

decreasing temperature. This is similar to the increase of the lattice constant *c* in the case of KAu(CN)$_2$.[1] On the other hand, the lattice parameters *a* and *c* appear to decrease nearly linearly and quadratically, respectively. As well, the unit cell volume indicates only a slight "saturation" to a minimum value at low temperatures. The *b*-parameter anomaly (increase) appears to be mainly related to a remarkably linear reorientation of the [Au(3)(CN)$_2$]⁻ ion, yielding a reduction of the tilt angle in the (*a,b*)-plane to the *b*-axis from approximately 50.7 to 47.6° as

TlAu(CN)$_2$
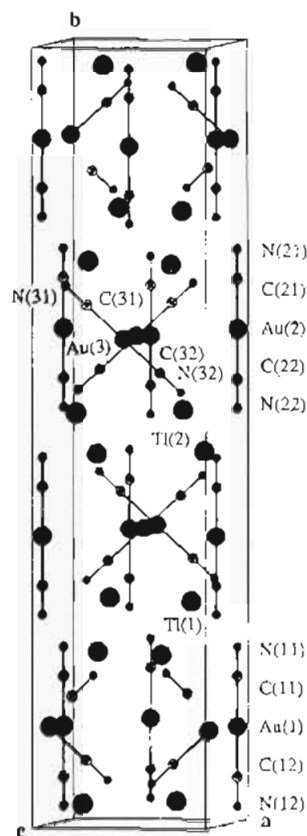
Figure 4. Unit cell plot of TlAu(CN)$_2$ for *T* = 5 K.
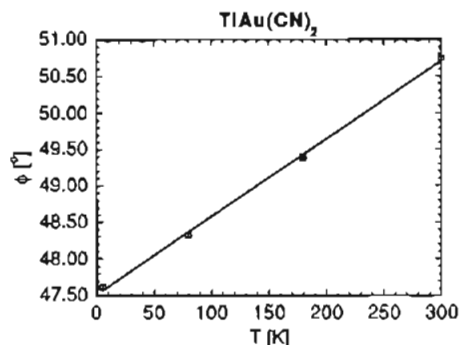
Figure 5. Linear temperature dependence of the tilt angle ϕ of the [Au(3)(CN)$_2$]⁻ ion with respect to the *b*-axis in the (*a,b*)-plane.

illustrated in Figure 5. With decreasing temperature, the [Au(3)(CN)$_2$]⁻ ion orients more and more parallel to the (*a,b*)-plane as it moves toward the *b*-axis. In addition, there are indications of minor reductions in Tl–N distances (such as Tl-(1)–N(11)—see Table 4) due to the lower temperature. Apart from the essential changes as a function of temperature the results confirm the room-temperature structure model of Blom et al. for TlAu(CN)$_2$.[3] The very anisotropic properties of TlAu(CN)$_2$ are presumably a consequence of rather rigid linear [Au(CN)$_2$]⁻ions. On the other hand, the temperature factors (in particular the ones of N(31) and N(32)) are remarkably large at room temperature, indicating considerable librational motions of the ions. The rather short distances Au(1)–Au(3) and Au(3)–Au-(3) decrease with decreasing temperature and approach (at 5 K) the value of approximately 2.9–3.0 Å. They indicate significant Au–Au overlap, as they are close to the value of the Au–Au distance of 2.88 Å in metallic Au.

Relativistically modified extended Hückel molecular orbital calculations for an isolated [Au(CN)$_2$]⁻ ion indicate that the highest occupied (HOMO) and lowest unoccupied (LUMO)

molecular orbitals are composed of Au ($5d_{z^2}$, 6s) and ($6p_x$, $6p_y$) atomic orbitals, respectively.[1,2] As two such ions are brought together, the HOMO–LUMO separation decreases consistent with the red shift in going from solution to the solid state. For the TlAu(CN)$_2$ salt, MO calculations for a Tl$^+$ ion close to a [Au(CN)$_2$]$^-$ ion indicates that the HOMO–LUMO separation is again decreased because of Tl–Au covalence.[2] Relativistic extended Hückel calculations for models of the three crystallographically distinguishable sites in Tl[Au(CN)$_2$] (see Table 2 of ref 2) suggest that the HOMO–LUMO separation is smallest along the Au(1)–Au(3) chain.

The optical luminescence data versus temperature for KAu(CN)$_2$ have been interpreted in terms of a Frenkel exciton model in which the luminescence energy E is given by the relation

$$E = E° - a/R^3 \qquad (1)$$

where $E°$ is the emission energy of an isolated [Au(CN)$_2$]$^-$ ion and R is the Au–Au nearest-neighbor separation.[1] An exciton results from an electron-hole pair in the presence of a lattice which varies in energy depending upon the HOMO–LUMO separation. Emission occurs when an electron and a hole recombine. For the KAu(CN)$_2$ salt, all of the Au ions are equivalent with a nearest-neighbor Au–Au room-temperature separation of 3.64 Å. A plot of the KAu(CN)$_2$ luminescence energy versus $1/R^3$ yielded a value of 43 800 cm^{-1} for $E°$ and 8.21 × 10^5 for the parameter a.[1] For TlAu(CN)$_2$, the observed luminescence has been assigned to electronic transitions localized along the Au(1)–Au(3) chain axis.[2] In Figure 6, the emission energy for TlAu(CN)$_2$ is plotted versus $1/R^3$ with R equal to the average Au–Au separation along the Au(1)–Au(3) chain axis. $E°$ is calculated in this case to be (4.2 ± 0.4) × 10^4 cm^{-1} and the parameter a is equal to (6 ± 1) × 10^5. The experimental value for $E°$ is estimated to be 42 000 cm^{-1} from the tetra-n-butylammonium dicyanoaurate(I) salt, where R is 8.04 Å at room

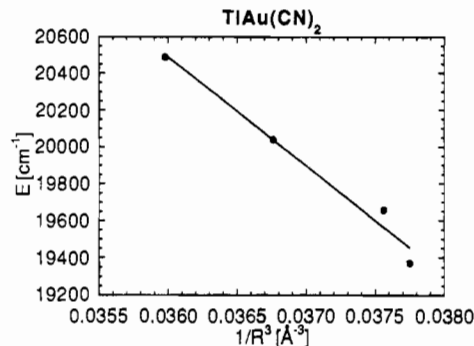**Figure 6.** Emission energy of TlAu(CN)$_2$ versus R^{-3}, where R is the average Au–Au separation along the Au(1)–Au(3) chain axis.

temperature.[9] The calculated value of $E°$ for TlAu(CN)$_2$ is in very good agreement with the experimental value. This supports the assignment that, in TlAu(CN)$_2$, the luminescence is from excitons localized along the Au(1)–Au(3) chain axis in contrast to the KAu(CN)$_2$ case where delocalization of the exciton occurs in Au–Au layers.

High-pressure neutron diffraction and optical measurements of these temperature-dependent properties of TlAu(CN)$_2$ and similar compounds will be important.

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