Inorg. Chem. **1997,** *36,* 2791−2794

Pressure Dependence Investigation of the Low-Temperature Structure of $TlAu(CN)_2$ by High-Resolution Neutron Powder Diffraction and Optical Studies

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Received November 22, 1996⊗

In contrast to the anomalous increase of the lattice parameter b and associated reorientation of the $[Au(3)(CN)_2]^-$ ion with decreasing temperature, the unit cell volume and the lattice parameters of $TlAu(CN)_2$ are found to decrease (at $T = 62$ K) linearly for external hydrostatic pressures up to 4.5 kbar. The $[Au(CN)_2]^-$ ions do not essentially change orientation with pressure. The structural results suggest that the change in luminescence energy with pressure is due to changes in Tl···Au as well as in Au···Au interatomic separations, which again illustrates the importance of Tl···Au covalent interactions in this compound.

Introduction

$TlAu(CN)_2$ is an inorganic compound crystallizing with a rather complex orthorhombic crystal structure, corresponding to space group *Pbcn*. The unit cell contains Tl^+ and three crystallographically nonequivalent $[Au(CN)_2]^-$ ions. An anomalous increase of the largest lattice parameter $b \approx 30$ Å with decreasing temperature was detected by means of high-resolution neutron powder diffraction.[1] It was found to be related to a reorientation of one of the three linear N−C−Au−C−N ions. As a basis for understanding corresponding optical investigations, it was therefore important to determine the influence of external hydrostatic pressure on the chemical structure in such a case. To a certain extent, pressure should diminish the lattice parameters and unit cell volume similar to temperature reduction. Here we shall report corresponding powder neutron diffraction experiments which were performed at ILL, Grenoble, France, on the D2B high-resolution neutron diffractometer, using a recently developed Ti−Zr "zero matrix" pressure cell. Surprisingly, the structural changes associated with pressure are found to differ essentially from those determined earlier as a function of temperature.[1]

Experimental Section

A new powder sample of $TlAu(CN)_2$ was prepared at the University of Berne, as described in ref 1. The specimen was first placed, under a helium gas atmosphere, in a cylindrical vanadium tube of 15 mm diameter and approximately 5 cm height. Under conditions similar to those described in ref 1, measurements were recorded at 5 K (atmospheric pressure) on the D2B neutron diffractometer, in the high-resolution mode, using the neutron wavelength $\lambda = 1.5943$ Å, to verify the single-phase quality of the new sample.

For the hydrostatic pressure measurements up to 4.5 kbar, the new Ti−Zr zero-matrix pressure cell with sample diameter ≈ 10 mm, cell diameter ≈ 23 mm, and sample height ≈ 30 mm was used. To avoid problems associated with solid helium, a temperature $T \approx 62$ K was chosen for the measurements. A first attempt of a high-resolution run with neutron wavelength $\lambda \approx 1.6$ Å was not continued because of insufficient intensity. Using the new pyrolytic graphite filter installed in the D2B diffractometer—eliminating higher order contaminations—neutron diffraction patterns were then measured with $\lambda = 2.3968$ Å at 0, 1.5, 3.0, and 4.5 kbar in the high-intensity mode of the D2B diffractometer (≈18 h per run). Thus, the Bragg peaks were sufficiently resolved to define the diffuse background originating mainly from incoherent scattering from the zero-matrix pressure cell. A corresponding neutron diffraction pattern of $TlAu(CN)_2$ is shown in Figure 1 for 4.5 kbar of hydrostatic pressure. Compared to previous pressure cells used at ILL the new cell yields an improvement in the peak-to-background ratio by an order of magnitude. On the other hand, the longer neutron wavelength leads to a reduced number of contributing Bragg reflections (481 nonequivalent {*hkl*} reflections in the scattering angle range up to 140° used in the profile refinements). To limit the number of parameters we therefore used chemical constraints in the refinements,[2,3] similar to those in ref 1.

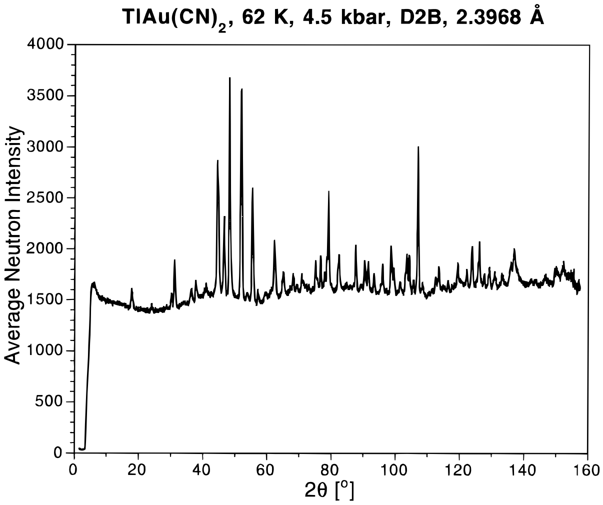
$TlAu(CN)_2$, 62 K, 4.5 kbar, D2B, 2.3968 Å

Figure 1. Neutron diffraction pattern of $TlAu(CN)_2$ at $T = 62$ K and $P = 4.5$ kbar (zero-matrix Ti−Zr pressure cell).

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⊗ Abstract published in *Advance ACS Abstracts*, May 15, 1997.

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S0020-1669(96)01405-X CCC: $14.00

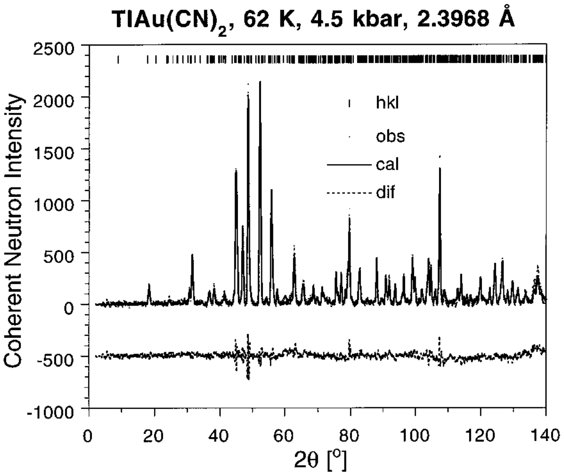

Figure 2. Count versus 2θ scan (observed (background subtracted), dots; calculated, full line, difference, lower dashed line) for neutron powder diffraction of $TlAu(CN)_2$ at 4.5 kbar and $T = 62$ K.

Data Analysis

The preliminary 5 K (atmospheric pressure) neutron powder diffraction data collected on the D2B diffractometer for $\lambda = 1.5943$ Å in the high-resolution mode were refined, and the agreement of the structure parameter values, within error limits, with those published in ref 1 was taken as confirmation of the single-phase quality of the new powder sample.

The neutron powder diffraction scans collected at an approximate temperature of 62 K and at pressures of 0, 1.5, 3.0, and 4.5 kbar were plotted. The various pressure scans were then adjusted to an effective common 2θ zero value with the 0 kbar scan data. The sample pressure cell did not cause additional Bragg diffraction lines but did cause a rather high, slowly varying background with the 2θ scattering angle. A number of discrete background height points were taken to allow subsequent background subtraction by interpolation during the later analysis procedure, and this process was repeated for each of the four pressure scans. A general structural model for $TlAu(CN)_2$ was proposed as previously by single-crystal neutron diffraction studies at room temperature[4] and later confirmed by neutron powder diffraction studies.[1] The compound has an orthorhombic crystal structure with space group *Pbcn*. There are three crystallographic nonequivalent$[Au(CN)_2]^-$ ions in the unit cell. Two of these N−C−Au−C−N ions are linear and are orientated parallel to the *b* axis, and the third is approximately linear, almost parallel to the *ab* plane and inclined at approximately 51° to the [010] direction, at room temperature. Layers of $[Au(CN)_2]^-$ ions alternate with layers of Tl^+ ions along the *b* axis.

For such a large pseudosymmetric structure, it was decided to analyze the powder diffraction patterns with chemical structural constraints using the MORGUE program.[2,3] Nuclear neutron scattering amplitudes were taken from Sears.[5] To limit the number of structural parameters, isotropic temperature factors were used, as this was considered a reasonable approximation at the sample temperature of approximately 62 K.

The initial positional parameter values were set at those reported in ref 1 for the sample at 5 K, and the instrumental parameter values were put equal to those refined at the same time, as all sets of data were collected on the D2B high-resolution neutron powder diffractometer.[6]

The structural models and details used in the refinements were as follows:

1. It was assumed that the two $[Au(CN)_2]^-$ ions parallel to the *b* axis could be treated as being linear and identical. The third $[Au(CN)_2]^-$ ion was considered linear also but almost parallel to the *ab* plane and inclined at an angle (approximately 51°) to the [010] direction, with dimensions possibly different from those of the other two ions. The model was refined for all four pressure data scans.

2. All three $[Au(CN)_2]^-$ ions were considered to be linear but not to have identical dimensions. Again the model was refined for all four pressure data scans.

3. The three $[Au(CN)_2]^-$ ions were considered to be strictly linear and identical, with constant bond lengths Au−C = 1.970 Å and C−N = 1.150 Å, held at the values previously obtained in a similar study investigating temperature dependency.[1] The model was refined for all four pressure data scans.

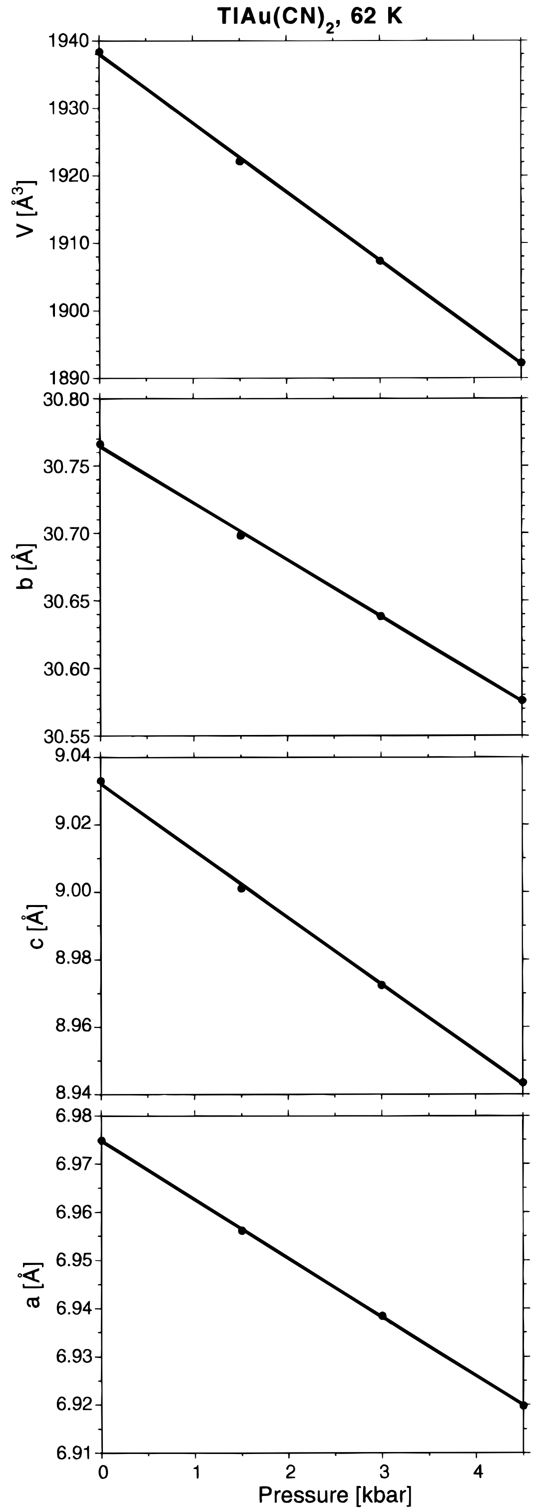

Figure 3. Pressure variation of lattice parameters and unit cell volume of $TlAu(CN)_2$ at $T = 62$ K. Error bars ($\delta a/a \approx \delta b/b \approx \delta c/c \approx 3 \times 10^{-5}$) of experimental values shown by symbols are within the symbol sizes. The lines represent linear fits.

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Table 1. Pressure P, Refinement Type, Number of Parameters Varied n_{par}, Residual Factors R_{wp} and R_{exp} for Weighted Profile Intensities and 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 $TlAu(CN)_2$, at Approximately 62 K

P (kbar)	refinement	n_{par}	R_{wp}	R_{exp}	χ^2	ϕ (deg)	θ (deg)
0	linear	26	13.89	7.86	3.12	48.00(3)	89.4(2)
	x,y,z	44	13.06	7.83	2.78		
1.5	linear	25	14.20	7.97	3.18	47.98(3)	89.2(2)
3.0	linear	25	15.22	8.06	3.57	48.15(4)	89.4(2)
4.5	linear	25	16.09	8.03	4.02	47.87(4)	90.8(2)

4. For the 0 kbar pressure data, a refinement starting at the constraint-refined values was attempted, but without any structural constraints.

(For models 1−3, the intraion group bond lengths and the "molecular" parameter values of center positions, the Euler angles, and the positional parameter values of Tl(1) and Tl(2) were refined. In addition, in all refinements the isotropic temperature factors of the Au, N, C, and Tl atoms were refined but constrained to be equal to others of same element type.)

Overall, it was found that model 3 with the three identical $[Au(CN)_2]^-$ ions gave essentially as good an agreement with the observed scan data as the other models but with the least number of variable parameters, and it was therefore considered the preferred structural model.

Neutron Diffraction Results

An illustrative neutron powder diffraction pattern of $TlAu(CN)_2$ for observed, calculated, and difference points is shown in Figure 2. The pressure dependence of the lattice parameters and unit cell volume are shown in Figure 3. The pressure dependence of the relevant "molecular" parameters and refinement details are given in Table 1. Positional parameters and isotropic temperature factors refined at 0, 1.5, 3.0, and 4.5 kbar pressure are given in Table 2. The shortest interatomic distances based on the values in Table 2 are given in Table 3.

Optical Results

The 60 K luminescence spectrum of $TlAu(CN)_2$ consists of a strong peak at 526 nm (19 000 cm^{-1}) when the substance is excited at 364 nm. Increasing the applied pressure from 0 to 4.5 kbar results[7] in a change of the luminescence energy of −140 cm^{-1}/kbar, or a decrease in luminescence energy of 630 cm^{-1}.

Discussion and Conclusion

In contrast to the anomalous increase of the lattice parameter b and associated reorientation of the $[Au(3)(CN)_2]^-$ ion with decreasing temperature, application of external hydrostatic pressure to $TlAu(CN)_2$ results in a linear decrease of all lattice parameters and of the unit cell volume and does not significantly change the orientation and geometrical configurations of the $[Au(CN)_2]^-$ ions within the accuracy of the present high-resolution powder neutron diffraction study.

Table 3 shows how interatomic distances change when increased pressure is applied to the $TlAu(CN)_2$ compound. A linear plot of interatomic distances versus applied pressure is shown in Figure 4, which illustrates main trends. Of the three Au···Au distances listed (Au(2)···Au(1), Au(3)···Au(1), and Au(3)···Au(3)), the second decreases most with increasing pressure (by $\approx -1 \times 10^{-2}$ Å/kbar) while the shortest interatomic distance, Au(3)···Au(3), remains approximately constant. Since the Au(3)···Au(3) interatomic distance at 0 kbar applied pressure has a value of 2.91 Å, which is close to the Au···Au distance in metallic Au of 2.88 Å, it is not surprising that the

Table 2. Positional Parameters[a] and Isotropic Temperature Factors[b] B Obtained from "Linear" Refinements at 0, 1.5, 3.0, and 4.5 kbar Pressure (in Vertical Sequence), at approximately 62 K

	x	y	z	B (Å^2)
Au(1)	0.0000	0.1237(33)	0.2500	1.24(11)
		0.1220(37)		1.38(11)
		0.1219(35)		1.33(12)
		0.1170(29)		1.21(12)
N(11)	0.0000	0.2251(33)	0.2500	2.13(8)
		0.2236(37)		2.19(9)
		0.2238(35)		2.18(9)
		0.2191(29)		2.45(10)
C(11)	0.0000	0.1877(33)	0.2500	1.41(10)
		0.1861(37)		1.44(10)
		0.1862(35)		1.29(10)
		0.1814(29)		1.70(11)
C(12)	0.0000	0.0597(33)	0.2500	
		0.0578(37)		
		0.0576(35)		
		0.0526(29)		
N(12)	0.0000	0.0223(33)	0.2500	
		0.0203(37)		
		0.0201(35)		
		0.0150(29)		
Au(2)	0.5000	0.1314(23)	0.2500	
		0.1315(27)		
		0.1326(25)		
		0.1285(35)		
N(21)	0.5000	0.2328(23)	0.2500	
		0.2331(27)		
		0.2344(25)		
		0.2305(35)		
C(21)	0.5000	0.1954(23)	0.2500	
		0.1957(27)		
		0.1969(25)		
		0.1929(35)		
C(22)	0.5000	0.0674(23)	0.2500	
		0.0673(27)		
		0.0683(25)		
		0.0641(35)		
N(22)	0.5000	0.0300(23)	0.2500	
		0.0299(27)		
		0.0308(25)		
		0.0264(35)		
Au(3)	0.4955(24)	0.3751(4)	0.4113(11)	
	0.4967(27)	0.3753(5)	0.4122(12)	
	0.4932(25)	0.3745(5)	0.4111(12)	
	0.5003(31)	0.3772(5)	0.4135(13)	
N(32)	0.8279(24)	0.4430(4)	0.4149(11)	
	0.8299(27)	0.4433(5)	0.4173(12)	
	0.8282(25)	0.4424(5)	0.4150(12)	
	0.8346(31)	0.4457(5)	0.4084(13)	
C(32)	0.7054(24)	0.4180(4)	0.4135(11)	
	0.7071(27)	0.4182(5)	0.4154(12)	
	0.7047(25)	0.4174(5)	0.4136(12)	
	0.7114(31)	0.4205(5)	0.4103(13)	
C(31)	0.2857(24)	0.3323(4)	0.4090(11)	
	0.2864(27)	0.3323(5)	0.4090(12)	
	0.2818(25)	0.3316(5)	0.4087(12)	
	0.2892(31)	0.3340(5)	0.4166(13)	
N(31)	0.1632(24)	0.3073(4)	0.4076(11)	
	0.1635(27)	0.3073(5)	0.4071(12)	
	0.1583(25)	0.3066(5)	0.4073(12)	
	0.1659(31)	0.3088(5)	0.4185(13)	
Tl(1)	0.7695(14)	0.2849(4)	0.4044(16)	1.28(13)
	0.7740(16)	0.2834(6)	0.4100(28)	1.58(13)
	0.7696(16)	0.2853(4)	0.4079(19)	1.09(13)
	0.7747(17)	0.2802(7)	0.4087(23)	1.45(15)
Tl(2)	0.2220(13)	0.4733(4)	0.4221(16)	
	0.2272(16)	0.4713(5)	0.4176(28)	
	0.2293(16)	0.4724(4)	0.4245(18)	
	0.2302(18)	0.4681(7)	0.4244(22)	

[a] Positional-parameter constraints applied such that all three $[Au(CN)_2]^-$ ions are considered identical with "linear" configuration and bond lengths held constant at Au - C = 1.970 Å and C - N = 1.150 Å. The centroidal and orientational positions of the $[Au(CN_2)]^-$ and positions of the Tl^+ ions, in addition to the constrained isotropic temperature factors were refined. [b] Temperature factor constraints are: B[Au(2)] = B[Au(1)] = B[Au(3)], B[C(31)] = B[C(32)] = B[C(22)] = B[C(21)] = B[C(12)] = B[C(11)], B[N(31)] = B[N(32)] = B[N(22)] = B[N(21)] = B[N(12)] = B[N(11)], and B[Tl(2)] = B[Tl(1)].

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Table 3. Selected Interatomic Distances (Å) in $TlAu(CN)_2$ as a Function of Pressure, Obtained from "Linear" $[Au(CN)_2]^-$ Ion Refinements, at approximately 62 K

	P (kbar)			
	0	1.5	3.0	4.5
Au(2)···Au(1)	3.496(8)	3.490(12)	3.485(12)	3.478(14)
Au(3)···Au(1)	3.060(10)	3.042(11)	3.043(11)	3.015(13)
Au(3)···Au(3)	2.914(14)	2.920(15)	2.892(15)	2.925(16)
Au(3)···Tl(1)	3.370(18)	3.418(23)	3.339(20)	3.522(26)
Au(3)···Tl(2)	3.574(18)	3.493(22)	3.516(20)	3.351(26)
Tl(1)···N(11)	2.813(67)	2.800(77)	2.848(72)	2.817(62)
Tl(1)···N(31)	2.831(19)	2.807(22)	2.775(21)	2.846(25)
Tl(2)···N(12)	2.906(54)	2.853(62)	2.849(57)	2.824(48)
Tl(2)···N(22)	2.803(46)	2.830(56)	2.861(50)	2.854(69)
Tl(2)···N(32)	2.904(19)	2.894(22)	2.932(21)	2.825(25)

Bond Distances (Å)

Au−C	1.970	C−N	1.150	Au−C−N	3.120

Au(3)···Au(3) distance does not decrease with increasing applied pressure. In contrast, the Au(3)···Tl(2) and Tl(2)···N(12) interatomic distances change, for example, by -5×10^{-2} and -2×10^{-2} Å/kbar, respectively.

The pressure-dependent structural results can be compared with the temperature-dependent structural results for $TlAu(CN)_2$ reported recently.[1] Plots of the listed interatomic distances in the latter publication versus temperature show that the Au···Au, Au···Tl, and Tl···N interatomic separations almost all change by $\approx 10^{-4}$ Å/K. Thus, temperature versus pressure changes for $TlAu(CN)_2$ result in different relative changes in Au···Au, Au···Tl, and Tl···N interatomic separations.

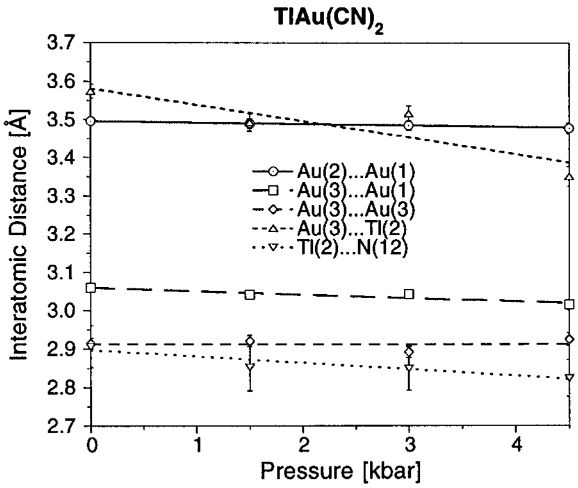

Figure 4. Plot of selected interatomic distances including straight-line fits for $TlAu(CN)_2$ versus pressure at $T = 62$ K.

Spectroscopic and electronic structure evidence for the existence of both Tl···Au and Au···Au covalent interactions in $TlAu(CN)_2$ was previously reported.[8] Relativistic effects are shown to play an important role in Tl···Au and Au···Au bonding. Further, the structural changes reported herein for $TlAu(CN)_2$ when pressure is applied between 0 and 4.5 kbar indicate larger changes in Tl···Au interatomic distances than in Au···Au interatomic distances. These results suggest that the change in luminescence energy with applied pressure, between at least 0 and 4.5 kbar, in $TlAu(CN)_2$ is due to changes in Tl···Au as well as Au···Au interatomic separations. This again shows the importance of Tl···Au covalent interactions in $TlAu(CN)_2$.

Acknowledgment. Expert technical support by L. Mélési, ILL, for the pressure measurements is gratefully acknowledged.

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