



## Article

# Syntheses and Characterization of Two Dicyanamide Compounds Containing Monovalent Cations: $\text{Hg}_2[\text{N}(\text{CN})_2]_2$ and $\text{Tl}[\text{N}(\text{CN})_2]$

Markus Mann <sup>1</sup>, Olaf Reckeweg <sup>1</sup> , Nils Nöthling <sup>2</sup> , Richard Goddard <sup>2</sup> and Richard Dronskowski <sup>1,\*</sup>

<sup>1</sup> Chair of Solid-State and Quantum Chemistry, Institute of Inorganic Chemistry, RWTH Aachen University, 52056 Aachen, Germany; markus.mann@ac.rwth-aachen.de (M.M.); olaf.reykjavik@gmx.de (O.R.)

<sup>2</sup> Max-Planck-Institut für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany; noethling@mpi-muelheim.mpg.de (N.N.); goddard@mpi-muelheim.mpg.de (R.G.)

\* Correspondence: drons@HAL9000.ac.rwth-aachen.de; Tel.: +49-241-809-3642; Fax: +49-241-809-2642

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**Abstract:** Crystals of  $\text{Hg}_2[\text{N}(\text{CN})_2]_2$  were grown by a slow diffusion-reaction between aqueous  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}[\text{N}(\text{CN})_2]$ .  $\text{Hg}_2[\text{N}(\text{CN})_2]_2$  adopts the triclinic space group  $P\bar{1}$  (no. 2) with  $a = 3.7089(5)$ ,  $b = 6.4098(6)$ ,  $c = 8.150(6)$  Å,  $\alpha = 81.575(6)^\circ$ ,  $\beta = 80.379(7)^\circ$ ,  $\gamma = 80.195(7)^\circ$ , and  $Z = 1$ . Crystals of  $\text{Tl}[\text{N}(\text{CN})_2]$  were obtained from the reaction of  $\text{TlBr}$  with  $\text{Ag}[\text{N}(\text{CN})_2]$  in water. Single-crystal structure analyses evidence that  $\text{Tl}[\text{N}(\text{CN})_2]$  is isotypic to  $\alpha\text{-K}[\text{N}(\text{CN})_2]$  and adopts the orthorhombic space group  $Pbcm$  (no. 57) with  $a = 8.5770(17)$ ,  $b = 6.4756(13)$ ,  $c = 7.2306(14)$  Å, and  $Z = 4$ . Regarding volume chemistry, the dicyanamide anion occupies ca.  $44 \text{ cm}^3 \cdot \text{mol}^{-1}$ , and so it corresponds to a large pseudohalide. The IR spectra of both compounds exhibit vibrational modes that are characteristic of the dicyanamide anion.

**Keywords:** dicyanamide; mercury; thallium; crystal structure; volume chemistry; IR spectrum; metathesis

## 1. Introduction

Nitrogen-based solid-state materials have found extremely diverse applications, for example, as simple fertilizers, as high-performance steel coatings, as III-V optical semiconductors, and, quite recently, even as lithium- and sodium-ion battery materials. In particular, complex nitrogen containing compounds beyond the simple, yet fundamental nitrides, such as carbodiimides or guanidates, are promising materials [1–3]. Similar to the latter in terms of chemical functionality, another interesting inorganic moiety is the boomerang-shaped dicyanamide anion  $[\text{N}(\text{CN})_2]^-$ , which is often dubbed as  $[\text{dca}]^-$ . It is intriguing, since it possesses one doubly-coordinated and two singly-coordinated nitrogen atoms plus several electron lone pairs.

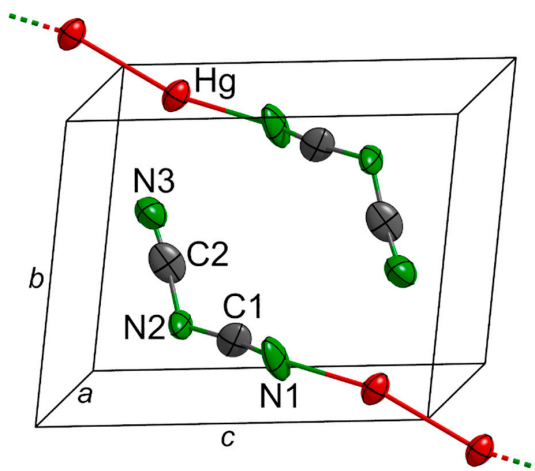
Generally speaking, the solubility of a metal dicyanamide in water is an important factor regarding the synthetic strategy of whatever binary or ternary phase is targeted. If the desired product is insoluble in water and can be filtered off after a metathesis reaction with  $\text{Na}[\text{dca}]$ , therefore this method can be used to grow crystals via a diffusion reaction. If the target compound is water soluble, however, it can be synthesized employing a metathesis reaction with  $\text{Ag}[\text{dca}]$ . In this case, the driving force for the reaction is the subsequent formation of insoluble silver halides. After filtering to remove the silver halides, the product can then be crystallized by simply evaporating water. Binary dicyanamide compounds are known for ammonium [4], alkali metals [5–8] (except Fr), alkaline-earth metals [9] (except Be and Ra), transition metals (Cr–Zn, except Fe) [10–16], and rare-earth metals (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) [17–19]. Ternary compounds, such as  $\text{KCs}[\text{dca}]_2$  [20],  $\text{LiK}[\text{dca}]_2$  [21],  $\text{LiRb}[\text{dca}]_2$  [21],  $\text{NaRb}_2[\text{dca}]_3 \cdot \text{H}_2\text{O}$  [20],  $\text{NaCs}_2[\text{dca}]_3$  [22], and  $\text{LiCs}_2[\text{dca}]_3$  [23] are also known.

The synthesis of  $\text{Hg}_2[\text{dca}]_2$  from  $\text{Hg}_2(\text{NO}_3)_2$  with  $\text{Na}[\text{dca}]$  has been reported almost a century ago [24], but no structural characterization was performed. Another attempt to characterize  $\text{Hg}_2[\text{dca}]_2$  by Kuhn and Mecke [25] in 1961 was based on IR data on a number of different dicyanamides. These measurements provided valid proof that the shape of the dicyanamide anion is kinked (or boomerang-shaped) instead of linear. Even though a working synthesis was known, no further investigations were made regarding the crystal structure of  $\text{Hg}_2[\text{dca}]_2$ . A further dicyanamide compound containing a monovalent cation with unknown crystal structure is  $\text{Tl}[\text{dca}]$ . Because of its high solubility in water,  $\text{Tl}[\text{dca}]$  cannot be synthesized analogously to  $\text{Hg}_2[\text{dca}]_2$ . The use of  $\text{Ag}[\text{dca}]$  provides a convenient alternative route to the crystals of  $\text{Tl}[\text{dca}]$ . We here report the syntheses and single-crystal structure determinations of  $\text{Hg}_2[\text{dca}]_2$  and  $\text{Tl}[\text{dca}]$ .

## 2. Results and Discussion

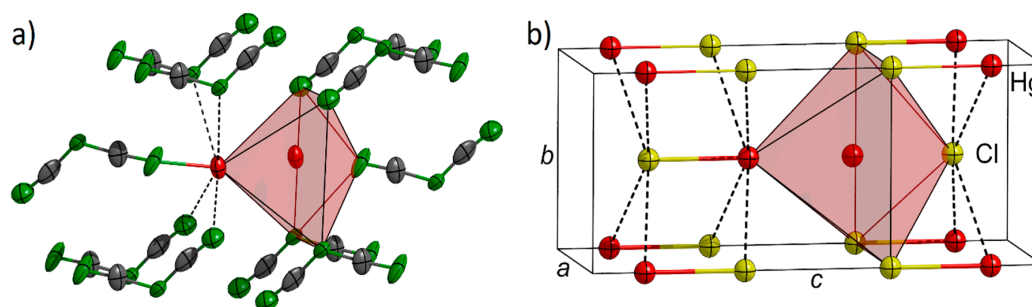
### 2.1. Structural Description and Discussion

$\text{Hg}_2[\text{N}(\text{CN})_2]_2$  adopts the triclinic space group  $P\bar{1}$  (no. 2) with  $a = 3.7089(5)$ ,  $b = 6.4098(6)$ ,  $c = 8.150(6)$  Å,  $\alpha = 81.575(6)^\circ$ ,  $\beta = 80.379(7)^\circ$ ,  $\gamma = 80.195(7)^\circ$ , and  $Z = 1$ . Similar to most Hg(I) compounds, crystalline  $\text{Hg}_2[\text{N}(\text{CN})_2]_2$  contains  $\text{Hg}_2$  moieties with  $d(\text{Hg}-\text{Hg}) = 2.518(3)$  Å. The structure can be compared to that of calomel,  $\text{Hg}_2\text{Cl}_2$ , where  $d(\text{Hg}-\text{Hg}) = 2.53$  Å [26]. In  $\text{Hg}_2[\text{dca}]_2$ , every  $\text{Hg}_2$  dumbbell is bonded to two [dca] anions forming a quasi-molecular  $\text{Hg}_2[\text{dca}]_2$  unit (Figure 1). A distorted octahedral coordination results for each Hg(I) due to four more coordinating nitrogen atoms. Therefore, every Hg(I) is surrounded by a total of five nitrogen belonging to five different [dca] anions, and also by the neighboring Hg(I) ion. Three of these dicyanamide anions coordinate the mercury ion with their terminal nitrogen atoms ( $d(\text{Hg}-\text{N1}) = 2.166(10)$ ,  $d(\text{Hg}-\text{N3}) = 2.612(12)$ , and  $d(\text{Hg}-\text{N3}) = 2.834(10)$  Å), whilst the others coordinate via their bridging nitrogen at a more distant  $d(\text{Hg}-\text{N2}) = 3.084(9)$  and  $3.412(22)$  Å. Similar distorted coordination octahedra are also known for  $\text{Hg}_2\text{Cl}_2$  [26] (Figure 2).

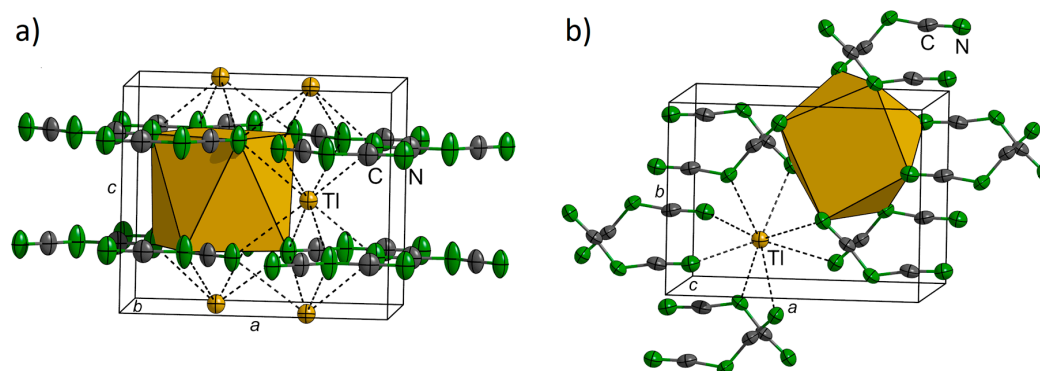


**Figure 1.** Crystal structure of  $\text{Hg}_2[\text{dca}]_2$ . The atomic displacement ellipsoids correspond to 90% probability using the refined anisotropic displacement parameters (ADPs).

$\text{Tl}[\text{dca}]$  crystallizes isotypically to  $\alpha\text{-K}[\text{dca}]$  and  $\alpha\text{-Rb}[\text{dca}]$  [7] in the orthorhombic space group  $Pbcm$  (no. 57) with  $a = 8.5770(17)$ ,  $b = 6.4756(13)$ ,  $c = 7.2306(14)$  Å, and  $Z = 4$ . This is not surprising due to the similar ionic radii of all three cations,  $\text{Tl}^+$ ,  $\text{K}^+$ , and  $\text{Rb}^+$ . The structure is built of layers of  $\text{Tl}^+$  and  $[\text{dca}]^-$ , in which  $\text{Tl}^+$  is coordinated by six terminal nitrogen atoms with  $d(\text{Tl}-\text{N1}) = 3.082(4)/3.089(4)$  and  $d(\text{Tl}-\text{N3}) = 2.870(4)$  Å and two bridging nitrogen atoms with  $d(\text{Tl}-\text{N2}) = 3.053(5)$  Å of eight different [dca] moieties, generating a distorted square antiprism (Figure 3). These Tl–N distances are in good agreement with those that were reported for a quadratic antiprismatic coordination polyhedron in  $\text{TlN}_3$  [27] with  $d(\text{Tl}-\text{N}) = 3.03$  Å.



**Figure 2.** Comparison of the crystal structures of  $\text{Hg}_2[\text{dca}]_2$  and calomel,  $\text{Hg}_2\text{Cl}_2$ . (a) Coordination sphere of Hg in  $\text{Hg}_2[\text{dca}]_2$ . The atomic displacement ellipsoids correspond to 90% probability using the refined ADPs. (b) Crystal structure of  $\text{Hg}_2\text{Cl}_2$  [26].



**Figure 3.** Crystal structure of  $\text{Tl}[\text{dca}]$  with (a) showing the view along  $c$  and (b) along  $b$ . The atomic displacement ellipsoids correspond to 90% probability using the refined ADPs.

Like before, the boomerang-shaped dicyanamide in  $\text{Tl}[\text{dca}]$  exhibits atomic distances and angles in the expected range: the bond length of  $d(\text{C1-N1}) = 1.148(8)$  and  $d(\text{C2-N3}) = 1.148(7)$  Å of the terminal C–N pairs indicate triple bonds, while the central C–N with  $d(\text{C1-N2}) = 1.316(8)$  and  $d(\text{C2-N2}) = 1.319(7)$  Å of the [dca] anion are also typically found for such a moiety, with  $\angle(\text{N1-C1-N2}) = 172.0(6)^\circ$ ,  $\angle(\text{N2-C2-N3}) = 172.6(6)^\circ$ , and  $\angle(\text{C1-N2-C2}) = 120.6(6)^\circ$  (Table 1).

**Table 1.** Selected angles ( $^\circ$ ) and bond lengths (Å) in  $\text{Hg}_2[\text{dca}]_2$  and  $\text{Tl}[\text{dca}]$ .

$\text{Hg}_2[\text{dca}]_2$	( $^\circ$ )	$\text{Tl}[\text{dca}]$	( $^\circ$ )
$\angle(\text{N1-C1-N2})$	171.6(14)	$\angle(\text{N1-C1-N2})$	172.0(6)
$\angle(\text{N2-C2-N3})$	173.2(13)	$\angle(\text{N2-C2-N3})$	172.6(6)
$\angle(\text{C1-N2-C2})$	119.4(10)	$\angle(\text{C1-N2-C2})$	120.6(5)
(Å)		(Å)	
N1–C1	1.148(14)	N1–C1	1.148(8)
C1–N2	1.325(13)	C1–N2	1.316(8)
N2–C2	1.317(16)	N2–C2	1.319(7)
C2–N3	1.108(16)	C2–N3	1.148(7)
Hg–Hg	2.518(3)	Tl–Tl ( $2\times$ )	3.6153(7)
Hg–N1	2.166(10)	Tl–Tl ( $2\times$ )	4.5129(7)
Hg–N2	3.412(11)	Tl–N1 ( $2\times$ )	3.089(4)
Hg–N2	3.084(9)	Tl–N1 ( $2\times$ )	3.082(4)
Hg–N3	2.612(12)	Tl–N2 ( $2\times$ )	3.053(5)
Hg–N3	2.834(10)	Tl–N3 ( $2\times$ )	2.870(4)

Given the large number of structurally characterized dicyanamides, it is tempting to finally investigate their volume chemistry. Hence, we calculated the volume increment of the dicyanamide anion according to the method of Biltz, that is, taking into account the tabulated volume increments [28]

of the monovalent cations  $M^+$ , namely those of Li, Na, K, Rb, Cs, Cu, Ag, Hg, Tl, and  $\text{NH}_4$ . As shown in Table 2, the dicyanamide anion has a volume of  $44.3(17) \text{ cm}^3 \cdot \text{mol}^{-1}$  on average, so it is about 70% larger than the  $\text{NCN}^{2-}$  cyanamide anion ( $26 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) [29]. That being said, the dicyanamide anion appears as a mid-heavy (66.04 u) but relatively spacious pseudohalide, and it finalizes the trend found [28] for the true halides ( $\text{F}^-$ : 9.5,  $\text{Cl}^-$ : 20,  $\text{Br}^-$ : 25,  $\text{I}^-$ : 34,  $[\text{dca}]^-$ :  $44 \text{ cm}^3 \cdot \text{mol}^{-1}$ ). For completeness, we add that the calculated  $[\text{dca}]^-$  volume increments for  $\text{Hg}_2[\text{dca}]_2$  and  $\text{Tl}[\text{dca}]$  (40.2 and  $41.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) appear as slightly smaller, which is probably due to the fact that these crystal structures were determined at a lower temperature (Table 2).

**Table 2.** Calculated molar volumes of  $[\text{dca}]^-$  based on  $M[\text{dca}]$  crystal structures containing monovalent cations.

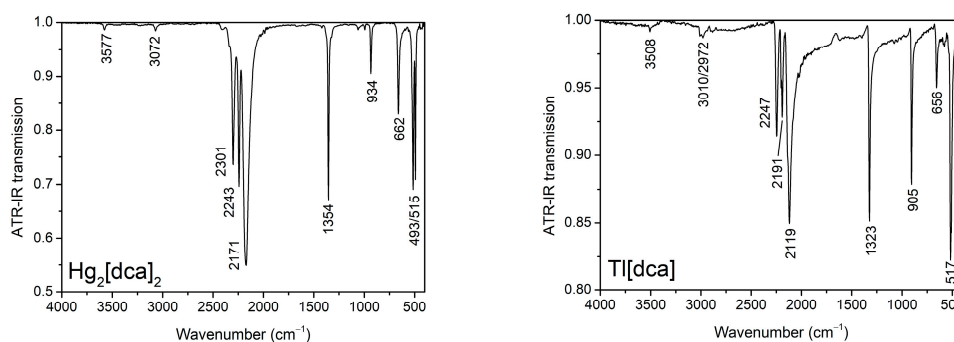
$M[\text{dca}]$	Cell Volume ( $\text{\AA}^3$ ), Z	$T$ (K)	Molar Volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$M^+$ Volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) [28]	$[\text{dca}]^-$ Volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )
$\text{NH}_4[\text{dca}]$ [4]	428.32, 4	200	64.5	19.5	45.0
$\text{Li}[\text{dca}]$ [5]	313.84, 4	170	47.2	1.5	45.7
$\text{Na}[\text{dca}]$ [8]	345.25, 4	293	52.0	6.5	45.5
$\alpha\text{-K}[\text{dca}]$ [7]	390.31, 4	293	58.7	16	42.7
$\beta\text{-K}[\text{dca}]$ [7]	416.78, 4	293	62.7	16	46.7
$\gamma\text{-K}[\text{dca}]$ [7]	415.56, 4	293	62.5	16	46.5
$\alpha\text{-Rb}[\text{dca}]$ [7]	433.4, 4	293	65.2	20	45.2
$\beta\text{-Rb}[\text{dca}]$ [7]	1778.31, 16	293	66.9	20	46.9
$\text{Cs}[\text{dca}]$ [6]	919.74, 8	299	69.2	26	43.2
$\text{Cu}[\text{dca}]$ [12]	332.21, 4	248	50.0	5	45.0
$\text{Ag}[\text{dca}]$ , o [14]	349.24, 4	293	52.6	9	43.6
$\text{Ag}[\text{dca}]$ , tr [14]	256.36, 3	293	51.4	9	42.4
$\text{Hg}_2[\text{dca}]_2$	186.84, 1	100	112.4	16	40.2
$\text{Tl}[\text{dca}]$	401.60, 4	100	60.4	18.5	41.9

## 2.2. IR-Spectra

The vibrational frequencies, as obtained from the IR spectra of the title compounds, confirm the presence of the  $[\text{dca}]$  group (Table 3, Figure 4).

**Table 3.** IR data of  $\text{Hg}_2[\text{dca}]_2$  and  $\text{Tl}[\text{dca}]$ . All numbers are given in  $\text{cm}^{-1}$ .

Vibration	$\nu(\text{Hg}_2[\text{dca}]_2)$	$\nu(\text{Tl}[\text{dca}])$
$\sigma_{\text{as}}(\text{N}-\text{C}\equiv\text{N})$	493/515	517
$\sigma_{\text{s}}(\text{N}-\text{C}\equiv\text{N})$	662	656
$\nu_{\text{s}}(\text{N}-\text{C})$	934	905
$\nu_{\text{as}}(\text{N}-\text{C})$	1354	1323
$\nu_{\text{as}}(\text{N}\equiv\text{C})$	2171	2119
$\nu_{\text{as}}(\text{N}-\text{C}) + \nu_{\text{s}}(\text{N}-\text{C})$	2243	2191
$\nu_{\text{s}}(\text{N}\equiv\text{C})$	2301	2247
$\nu_{\text{as}}(\text{N}\equiv\text{C}) + \nu_{\text{s}}(\text{N}-\text{C})$	3072	3010/2972
$\nu_{\text{s}}(\text{N}\equiv\text{C}) + \nu_{\text{as}}(\text{N}-\text{C})$	3577	3508



**Figure 4.** Infrared spectra of  $\text{Hg}_2[\text{dca}]_2$  (left) and  $\text{Tl}[\text{dca}]$  (right).

### 3. Materials and Methods

#### 3.1. Syntheses

Crystalline powder of  $\text{Hg}_2[\text{dca}]_2$  was synthesized by mixing stoichiometric amounts of  $\text{Na}[\text{dca}]$  and  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in water, followed by precipitation, but the fine powder was unsuitable for single-crystal diffraction. Better crystals of  $\text{Hg}_2[\text{dca}]_2$  were subsequently obtained by a diffusion reaction. An aqueous solution of  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (5 mL,  $c = 0.05$  M) was layered below, and another aqueous solution of  $\text{Na}[\text{dca}]$  (5 mL,  $c = 0.1$  M) was layered above an aqueous solution of  $\text{NaNO}_3$  (5 mL,  $c = 0.22$  M) in a regular test-tube. Colorless, transparent crystals of  $\text{Hg}_2[\text{dca}]_2$  grew within two days in the region between the layers of  $\text{Hg}_2(\text{NO}_3)_2$  and  $\text{NaNO}_3$ .

$\text{Tl}[\text{dca}]$  was obtained by adding  $\text{TlBr}$  (184.8 mg, 0.65 mmol) to an aqueous  $\text{Ag}[\text{dca}]$  (120.5 mg, 0.69 mmol, 5 mL deionized  $\text{H}_2\text{O}$ ) suspension. The synthesis of  $\text{Ag}[\text{dca}]$  has been described in a previous paper [23]. The suspension was stirred for twelve hours under the exclusion of light. 1 mL of the silver bromide-free solution was taken, and the water was evaporated in a desiccator. A colorless, transparent, orthorhombic crystal of  $\text{Tl}[\text{dca}]$  suitable for single-crystal X-ray diffraction was selected for diffraction data collection.

#### 3.2. Single Crystal Diffraction

A suitable single crystal of  $\text{Hg}_2[\text{dca}]_2$  was mounted on a glass fiber. Intensity data were collected with a STOE STADIVARI Dectris Pilatus 200K detector (STOE & Cie GmbH, Darmstadt, Germany), equipped with a GeniX Mo High Flux source (Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å, multilayer optics). Temperature control was achieved using an Oxford Cryostream 800 (Oxford Cryosystems Ltd., Oxford, UK) at 100 K. Collected data were integrated with X-Area Integrate [30], and Gaussian-integration absorption corrections were applied with STOE X-Red [31]. The structure was solved by charge-flipping methods (Superflip [32]) and refined on  $F^2$ , as implemented in Jana2006 [33]. More crystallographic details can be found in Tables 4–6. The goodness-of-fit is unusually large (3.60) and it probably goes back to the rather high absorption coefficient for Mo  $K\alpha$  radiation resulting in an imperfect absorption model.

**Table 4.** Summary of single-crystal X-ray diffraction structure determination data of  $\text{Tl}[\text{dca}]$  and  $\text{Hg}_2[\text{dca}]_2$ .

Chemical Formula	$\text{Hg}_2[\text{dca}]_2$	$\text{Tl}[\text{dca}]$
Formula weight ( $\text{g} \cdot \text{mol}^{-1}$ )	533.3	270.42
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$ (no. 2)	$Pbcm$ (no. 57)
Temperature (K)	100(2)	100(2)
$a$ (Å)	3.7089(5)	8.5770(17)
$b$ (Å)	6.4098(6)	6.4756(13)
$c$ (Å)	8.150(6)	7.2306(14)
$\alpha$ (°)	81.575(6)	90
$\beta$ (°)	80.379(7)	90
$\gamma$ (°)	80.195(7)	90
$V$ (Å <sup>3</sup> )	186.84(14)	401.60(14)
$Z$	1	4
Radiation, $\lambda$ (Å)	Mo $K\alpha$ , 0.71073	Mo $K\alpha$ , 0.71073
$\mu$ ( $\text{mm}^{-1}$ )	41.09	40.022
Crystal shape and color	Colorless block	Colorless block
Crystal size ( $\text{mm}^3$ )	$0.17 \times 0.08 \times 0.02$	$0.05 \times 0.04 \times 0.02$
$\rho_{\text{calcd}}$ ( $\text{g} \cdot \text{cm}^{-3}$ )	4.739	4.473
Diffractometer	STOE STADIVARI with Hybrid Pixel Counting Detector	Bruker AXS Enraf-Nonius with KappaCCD Detector
Absorption correction	Gaussian Integration, STOE X-RED	Gaussian Integration, SADABS 2014/15

Table 4. Cont.

Chemical Formula	Hg <sub>2</sub> [dca] <sub>2</sub>	Tl[dca]
$T_{\min}, T_{\max}$	0.0672, 0.6730	0.15236, 0.46282
No. of measured,	3671	8880
independent and observed	1263	816
$[I > 3\sigma(I)]$ reflections	1154	549
$R_{\text{obs}}$	4.68	1.87
$wR2_{\text{obs}}$	10.88	3.94
$R_{\text{all}}$	4.92	3.25
$wR2_{\text{all}}$	10.91	4.46
$\text{GOF}_{\text{obs}}$	3.60	1.09
No. of parameters, restraints	55, 0	36, 0

Table 5. Atomic coordinates (all on 2i) and equivalent isotropic displacement parameters  $U_{\text{eq}}$  ( $\text{\AA}^2$ ) of Hg<sub>2</sub>[dca]<sub>2</sub>.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Hg	0.96205(10)	0.90300(6)	0.14632(4)	0.01463(12)
N1	0.923(3)	0.805(2)	0.4137(12)	0.024(3)
N2	0.619(3)	0.7427(15)	0.7062(10)	0.015(2)
N3	0.406(3)	0.4138(17)	0.8391(12)	0.020(3)
C1	0.765(3)	0.7693(19)	0.5460(13)	0.016(3)
C2	0.510(3)	0.559(2)	0.7710(14)	0.018(3)

Table 6. Anisotropic displacement parameters  $U_{ij}$  ( $\text{\AA}^2$ ) of Hg<sub>2</sub>[dca]<sub>2</sub>.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Hg	0.01303(19)	0.0173(2)	0.01206(19)	−0.00301(13)	0.00010(12)	0.00189(13)
N1	0.026(5)	0.038(6)	0.011(4)	−0.014(4)	0.005(3)	−0.012(4)
N2	0.023(4)	0.012(4)	0.009(3)	0.001(3)	−0.001(3)	−0.004(3)
N3	0.025(5)	0.018(5)	0.018(4)	−0.005(4)	−0.002(3)	−0.006(3)
C1	0.008(4)	0.022(5)	0.018(4)	−0.005(4)	0.000(3)	0.000(4)
C2	0.006(4)	0.027(6)	0.020(5)	−0.002(4)	0.004(3)	−0.010(4)

A suitable single crystal of Tl[dca] was adhered to a 100  $\mu\text{m}$  MiTeGen loop using perfluoropolyether PFO-XR75. Intensity data were collected on a FR 591 rotating anode that was equipped with an Incoatec Helios focusing multilayer optic (Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) and a Bruker AXS Enraf-Nonius KappaCCD detector (Bruker AXS GmbH, Karlsruhe, Germany). The temperature of the crystal was maintained at 100 K using an Oxford Cryostream 700 (Oxford Cryosystems Ltd., Oxford, United Kingdom). Diffraction data were integrated with the program REVALCCD ver. 1.6, 2008 and a Gaussian integration absorption correction based on the crystal shape was applied using SADABS [34]. Data preparation and reciprocal space exploration were performed by XPREP [35]. The structure was solved with SHELXT [36] by a dual-space method and was refined on  $F^2$ , as implemented in SHELXL [37]. Crystallographic details can be found in Tables 4, 7 and 8.

Additional details concerning the structure determination are available in CIF format (see Supplementary Materials) and have been deposited under the CCDC entry numbers 1881933 for Tl[dca] and 1881934 for Hg<sub>2</sub>[dca]<sub>2</sub>. Copies of the data can be obtained free of charge from CCDC (<http://www.ccdc.cam.ac.uk/conts/retrieving.html>).

Table 7. Atomic coordinates and equivalent isotropic displacement parameters  $U_{\text{eq}}$  ( $\text{\AA}^2$ ) of Tl[dca].

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Tl	4c	0.31674(2)	1/4	1/2	0.01287(6)
N1	4d	0.5898(6)	0.3835(8)	3/4	0.0183(10)
N2	4d	0.7848(7)	0.1054(9)	3/4	0.0218(12)
N3	4d	0.0707(6)	0.1391(8)	3/4	0.0194(10)
C1	4d	0.6880(5)	0.2630(11)	3/4	0.0144(10)
C2	4d	0.9369(7)	0.1356(9)	3/4	0.0150(10)



**Table 8.** Anisotropic displacement parameters  $U_{ij}$  ( $\text{\AA}^2$ ) of Tl[dca].

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Tl	0.01236(9)	0.01241(10)	0.01384(9)	−0.00016(13)	0	0
N1	0.0111(19)	0.013(2)	0.031(3)	0	0	−0.002(2)
N2	0.012(2)	0.010(2)	0.043(4)	0	0	−0.003(2)
N3	0.015(2)	0.012(2)	0.031(3)	0	0	0.0007(19)
C1	0.012(2)	0.009(3)	0.022(3)	0	0	−0.003(3)
C2	0.017(3)	0.008(2)	0.020(3)	0	0	−0.002(2)

### 3.3. Infrared Spectra

The IR spectra were recorded using an ALPHA II FT-IR-spectrometer (Bruker Optik GmbH, Ettlingen, Germany), equipped with an ATR Platinum Diamond measuring cell. All measurements were undertaken within the range of 4000 to 400  $\text{cm}^{-1}$ .

## 4. Conclusions

The compounds  $\text{Hg}_2[\text{dca}]_2$  and  $\text{Tl}[\text{dca}]$  were synthesized, their respective crystal structures were determined, and their IR spectra were measured. While the structure of  $\text{Hg}_2[\text{dca}]_2$  shows similarities to the structure of  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Tl}[\text{dca}]$  is isostructural to  $\alpha\text{-K}[\text{dca}]$  and  $\alpha\text{-Rb}[\text{dca}]$ . The  $[\text{dca}]^-$  pseudohalide exceeds  $\text{I}^-$  in its volume increment. The acquired data of the IR spectra are similar to the data of the previously reported dicyanamides.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2304-6740/6/4/135/s1>: CIF and CIFchecked files.

**Author Contributions:** M.M. and O.R. conceived and designed the experiment; M.M. performed the syntheses, ATR-IR experiments and the single-crystal X-ray diffraction (SXRD) of  $\text{Hg}_2[\text{dca}]_2$ ; N.N. and R.G. performed the SXRD of  $\text{Tl}[\text{dca}]$ ; results were discussed with all authors; M.M. wrote the paper in collaboration with all co-authors.

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