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ARTICLE

Synthesis and Structural Investigation of a Complete Series of Brightly Colored Alkali Metal 1,3-Dimethylviolurates

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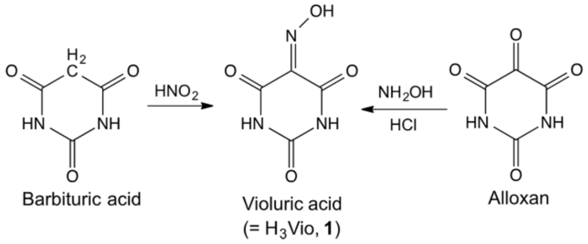
Dedicated to Professor Herbert W. Roesky on the Occasion of his 85th Birthday

Abstract. A complete series of alkali metal 1,3-dimethylviolurates $M(Me_2Vio)$ was synthesized and fully characterized. The title compounds $M(Me_2Vio)(H_2O)$ [M = Li (**3**), Na (**4**)], $K(Me_2Vio)(H_2O)_{0.5}$ (**5**) and $M(Me_2Vio)$ [M = Rb (**6**), Cs (**7**)] were prepared by neutralizing 1,3-dimethylvioluric acid (= HMe_2Vio; **2**) with 1 equiv. of the corresponding metal hydroxides MOH. The resulting salts exhibit striking colors ranging from orange-red (**3**) through purple (**4**, **5**) to bright blue (**6**, **7**). In contrast to the monohydrate **4**, the classical synthesis of sodium 1,3-dimethylviolurate from 1,3-dimethylbarbituric acid and $NaNO_2$ afforded the purple trihydrate $Na(Me_2Vio)(H_2O)_3$ (**4a**). All new compounds have been fully characterized by their IR and NMR (^1H, ^{13}C) spectra as well as elemental analyses. X-ray crystal structure determination revealed that the title compounds exist as one- (Li, Na), two- (K, Cs), or three-dimensional (Rb) coordination polymers in the solid state.

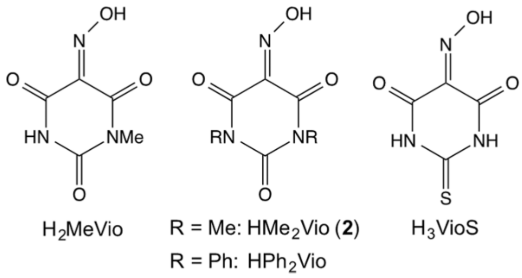
Introduction

Violuric acid (= H_3Vio; **1**) (other names are 2,4,5,6(1*H*,3*H*)-pyrimidinetetrone-5-oxime, alloxan-5-oxime, 5-(hydroxyimino)barbituric acid, and 5-isonitrosobarbituric acid) is a fascinating small molecule, which was first described over 150 years ago by *Adolf Baeyer* as part of his famous investigations on uric acid and its derivatives.[1–3] As illustrated in Scheme 1 (left), Baeyer's original preparation of violuric acid involved the reaction of barbituric acid with HNO_2 to generate the oxime functionality.[1–5] Today, violuric acid is normally prepared in high yields through the reaction of alloxan with hydroxylamine hydrochloride (Scheme 1, right).[6,7] Violuric acid is also commercially available in the form of its monohydrate. A rather unique feature of violuric acid is the so-called pantochromism. This is the effect that salt formation of *colorless* violuric acid with *colorless* cations such as alkali and alkaline earth metal ions, NH_4^+ or organoammonium cations results in the formation of brightly colored salts (e.g. red, blue and purple).[8] Pantochromic salts of violuric acid with alkali metal salts have been investigated more than 100 years ago by *Hantzsch* and co-workers[9–13] and more recently by different other authors.[14–16] Structurally characterized examples include e.g. ammonium violurate[17] as well as potassium and rubidium violurate.[18] The occurrence of such spectacular colors in violurate salts has been attributed to an n → π* transition of the violurate anion.[15] Other classes of organic compounds showing this phenomenon include e.g. 6-amino-5-nitrosouracil (= imidovioluric acid),[19–21] isonitrosomalonamide,[22] oximidoketones,[13] and oximido-oxazolones.[7,10,23–25]



Scheme 1. Preparative routes to violuric acid (**1**).

As shown in Scheme 2, several modifications of the parent violuric molecule are known, including 1-methylvioluric acid, 1,3-dimethylvioluric acid (**2**) and 1,3-diphenylvioluric acid, as well as 2-thiovioluric acid.



Scheme 2. Important derivatives of violuric acid.

The coordination chemistry of violuric acid and its derivatives has recently been surveyed in a comprehensive review

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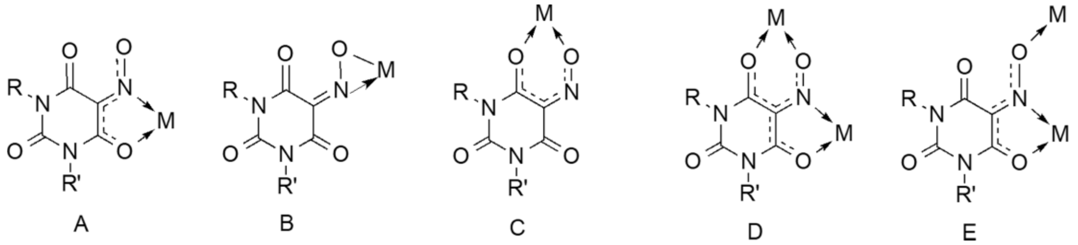


Scheme 3. Coordination modes of violurate anions. (a) *N*,*O*-bidentate, κ*N*,*O*; (b) η^2-NO; (c) *O*,*O*-bidentate, κ*O*,*O*′; (d) bis(bidentate)-bridging, κ*N*,*O*:κ*O*′,*O*′′; (e) tridentate bridging, κ*N*,*O*:κ*O*′′; R, R' = H, Me, and Ph.

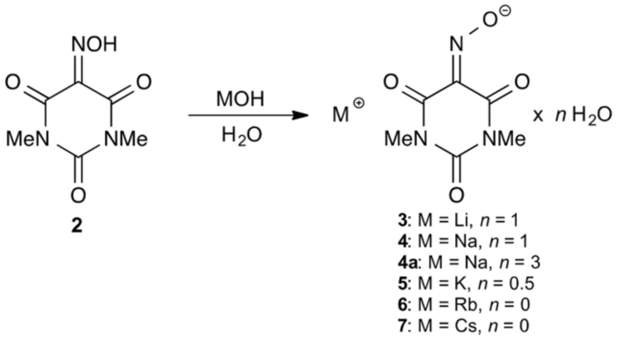
article.[26] In addition to the pantochromic salts mentioned above, violurate ligands also form various main group and transition metal complexes. More recent studies in this field showed that violurate ligands are versatile building blocks in supramolecular coordination compounds. Hydrogen-bonded 1D, 2D and 3D assemblies are possible in the crystalline state. In their metal complexes, violurate anions generally act as chelating and/or bridging ligands. Scheme 3 illustrates the bi- and tridentate chelating coordination modes which have been found so far. The most common type of metal-violurate coordination is the *N*,*O*-chelating mode shown in Scheme 3A. In this case a five-membered chelate ring is formed through coordination of the N atom of the oxime functionality and a neighboring carbonyl O atom to the metal. In contrast, there are only very few well-documented examples for other coordination modes, including η^2-coordination of the nitroso moiety (B), six-membered ring formation through κ-*O*,*O*′-chelation (C), and different bridging modes (D, E).[26]

Pantochromic behavior is also exhibited by virtually all salts and metal complexes derived from 1,3-dimethylvioluric acid (**2**). The complete series of alkali metal salts of **2** has already been reported by *Hantzsch* and *Robison* in the year 1910.[27] In the course of this early work, characterization of the compounds was limited to elemental analyses and UV/Vis spectra. We report here a modified synthesis and full characterization of the complete series of alkali metal 1,3-dimethylviolurates as well as their molecular and crystal structures as determined by single-crystal X-ray diffraction.

Results and Discussion

Preparation and Properties

As illustrated in Scheme 4, the title compounds were prepared in a simple and straightforward manner based on the original *Hantzsch* and *Robison* method[27] by neutralizing free 1,3-dimethylvioluric acid **2** (as monohydrate) with 1 equiv. of the respective metal hydroxide in ethanol. Under these conditions, orange-red Li(Me$_2$Vio)(H$_2$O) (**3**) crystallized from the reaction mixture upon standing at room temperature. Pink-violet Na(Me$_2$Vio)(H$_2$O) (**4**) was prepared analogously. The sodium salt **4** has a significantly lighter color than the previously reported trihydrate Na(Me$_2$Vio)(H$_2$O)$_3$ (**4a**) which forms glistening, dark red-purple crystals. Compound **4a** was prepared according to a published procedure by treatment of 1,3-dimethylbarbituric acid with NaNO$_2$.[28] Notably, this is a rather spectacular reaction. Mixing aqueous solutions of the colorless starting materials leads to formation of an intensely purple reaction mixture and rapid deposition of beautifully crystalline red-purple **4a**. The bluish-purple potassium salt was found to contain 0.5 equiv. of water of crystallization (K(Me$_2$Vio)(H$_2$O)$_{0,5}$, **5**).



Scheme 4. Synthesis of the title compounds **3**–**7**.

Figure 1 illustrates the characteristic solid-state colors of all title compounds **3**–**7**. Similar to the previously reported organoammonium violurates[29] the bright colors of the crystals range from orange-red to blue.

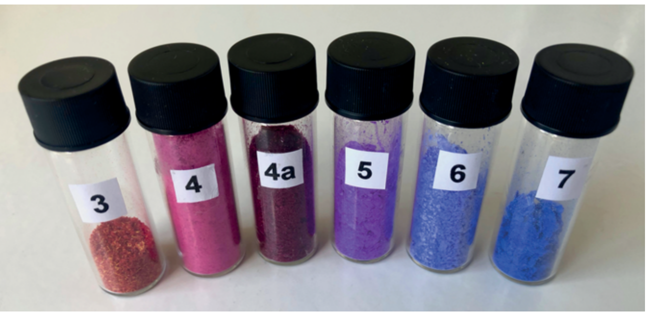


Figure 1. Characteristic colors of the title compounds **3**–**7** in the solid state.

All new compounds were fully characterized through IR, ^{1}H NMR and ^{13}C NMR spectroscopy as well as elemental analyses. In the IR spectra, the most prominent bands could be readily assigned.[30] The IR spectrum of **3** showed a broad band around 3490 cm^{-1}, which is assigned to ν(O–H). The stretching vibrational bands for C–H were observed at 2962 cm^{-1} and for the C=O bonds at 1720 and 1613 cm^{-1}.[31] The ν(N–O) vibration gives rise to a band at 1463 cm^{-1}. For compound **4a** the IR spectrum displays two H$_2$O bands at 3558 and 3515 cm^{-1}. The ν(C–H) band appears at 2967 cm^{-1}. For the carbonyl vibrations, three different bands at 1701, 1672 and 1626 cm^{-1} and for the N–O group at 1460 cm^{-1} were found. In the potassium derivative **5**, the ν(O–H) appears at 3479 cm^{-1} and the ν(C–H) at 2966 cm^{-1}. For the three different C=O groups the vibrations were observed at 1718, 1709 and 1634 cm^{-1}, and the ν(N=O) was detected at 1466 cm^{-1}. The IR spectra of complexes **6** and **7** are very similar. The observed band at 3325 cm^{-1} is an indication for hygroscopic behavior. Both compounds show ν(C=O) vibrations at 1717 and 1632 cm^{-1} for **6** and 1706 and 1617 cm^{-1} for **7**. The broad band at 1464 cm^{-1} in **6** and 1470 cm^{-1} in **7** were attributed to the ν(N–O) vibration.

The ^{1}H NMR spectra for all investigated compounds, measured in D_2O, showed two signals for the chemically inequivalent methyl groups bound to nitrogen. The ^{13}C NMR spectra are also very similar within the series. The carbonyl groups between the nitrogen atoms were detected at δ = 167 ppm, whereas the *C*=O groups neighboring the *C*=N bond appeared at δ = 154 ppm and the *C*=N moiety at δ = 146 ppm.

Crystal Structures

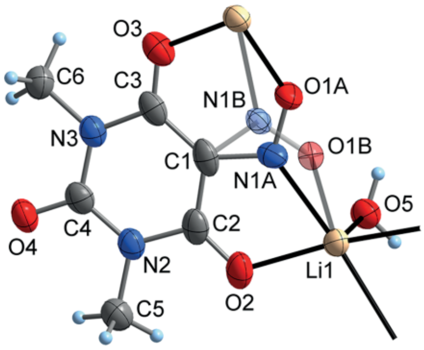


Figure 2. The asymmetric unit in the crystal structure of Li(Me$_2$Vio)(H$_2$O) (**3**), showing the atom numbering scheme and disorder of the nitroso group. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

Details on the crystallization of the title compounds are described in the Experimental Section. The crystallographic data of compounds **3**, **4a** and **5**–**7** are summarized in Table 1. Figure 2 and Figure 3 depict the molecular structure of the lithium salt **3**. In this compound, the Me$_2$Vio$^-$ anion adopts a dual-chelating κ^2*N*,*O*:κ^2*O*′,*O*′′-mode involving two symmetry-equivalent Li atoms (cf. pattern D in Scheme 3). The Li–O bond lengths are in a range of 194.8(6)–206.2(6) pm, and the Li–N bond is considerably longer at 220(1) pm. The two Me$_2$Vio$^-$ ligands at a specific Li atom are oriented almost coplanar, and an additional H_2O ligand defines the apex of a distorted square pyramid [coordination angles between neighboring donor atoms within base area: 70.2(3)–105.7(4)°]. This connectivity pattern results in the formation of infinite chains

Table 1. Crystallographic details for compounds **3**–**7**.

	3	4a	5	6	7
Molecular formula sum	$C_6H_8LiN_3O_5$	$C_6H_{12}N_3NaO_7$	$C_{12}H_{14}K_2N_6O_9$	$C_6H_6N_3O_4Rb$	$C_6H_6CsN_3O_4$
Formula weight /g·mol^{-1}	209.09	261.18	464.49	269.61	317.05
Crystal system	monoclinic	monoclinic	monoclinic	trigonal	orthorhombic
Space group	$P2_1/c$	$P2_1/m$	$P2_1/n$	R3*c*	P*na*2$_1$
Cell parameters					
a /Å	9.7641(6)	8.3203(5)	7.1517(3)	25.4890(7)	14.9958(5)
b /Å	10.1085(5)	6.9907(5)	31.850(1)	25.4890(7)	4.5329(2)
c /Å	8.6822(5)	9.4976(5)	8.3097(4)	6.7056(2)	25.9353(8)
α /°	90	90	90	90	90
β /°	91.006(5)	108.094(4)	113.863(3)	90	90
γ /°	90	90	90	120	90
Cell volume /Å^3	856.80(8)	525.11(6)	1731.0(1)	3772.9(2)	1762.9(1)
Molecules per cell *Z*	4	2	4	18	8
Calcd. density ρ /g·cm^{-3}	1.621	1.652	1.782	2.136	2.389
Absorption coefficient μ /mm^{-1}	0.139	0.182	0.614	5.898	4.194
Absorption correction	none	none	numerical [35]	numerical [35]	numerical [35]
Crystal color and shape	orange-red prism	purple plate	violet plate	blue rod	blue needle
Crystal size /mm	0.34 × 0.18 × 0.15	0.29 × 0.28 × 0.03	0.29 × 0.12 × 0.04	0.30 × 0.11 × 0.09	0.37 × 0.07 × 0.06
Temperature /K	133(2)	153(2)	133(2)	133(2)	133(2)
θ range /°	2.901 to 25.997	2.575 to 26.998	2.558 to 25.687	2.768 to 27.981	2.717 to 27.314
Reflections collected	5922	3390	10200	11472	9224
Reflections unique	1685	1235	3255	2005	3454
Reflections with $I > 2\sigma(I)$	1462	1001	2684	1947	3239
Completeness of dataset	99.7 %	99.6 %	99.9 %	99.3 %	99.7 %
R_{int}	0.0471	0.0465	0.0581	0.0591	0.0378
Parameters / restraints	164 / 2	116 / 4	272 / 2	130 / 1	258, 1
R_1 (all data, $I > 2\sigma(I)$)	0.0760, 0.0684	0.0514, 0.0365	0.0572, 0.0413	0.0323, 0.0303	0.0283, 0.0252
wR_2 (all data, $I > 2\sigma(I)$)	0.1744, 0.1685	0.0911, 0.0842	0.1074, 0.0964	0.0778, 0.0756	0.0618, 0.0601
GooF (F^2)	1.138	1.037	1.110	1.054	1.073
Extinction coefficient	0.063(9)	–	–	0.0006(2)	–
Largest diff. peak / hole	0.224 / –0.292	0.298 / –0.279	0.305 / –0.463	0.546 / –1.256	0.676 / –0.952
Flack parameter [34]	–	–	–	–0.031(8)	0.43(4) [a]

a) Refined as an inversion twin.

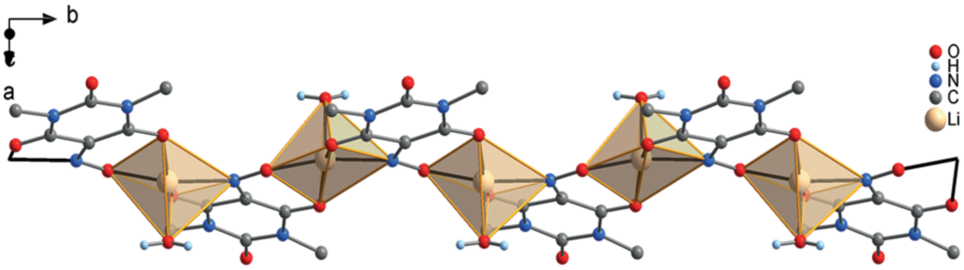


Figure 3. Polymeric chains in the crystal structure of **3**, extending along the crystallographic *b* axis.

of alternating Me_2Vio^- anions and $Li(H_2O)^+$ units. While the formation of five-membered rings through κ^2*N*,*O*-coordination is relatively rare in related lithium complexes, six-membered-ring formation through κ^2*O*,*O'*-coordination has frequently observed, e.g. in *ortho*-nitrophenolates.[32,33]

The asymmetric unit of the sodium derivative **4a** contains 0.5 formula units $Na(Me_2Vio)$ and 1.5 H_2O ligands (Figure 4). In this compound, the dimethylviolurate ligand adopts an unusual κ*O*:κ*O*-bridging coordination via the carbonyl group in 2-position, whereas the nitroso group and the remaining two carbonyl groups do not contribute to metal coordination. The Na atom is coordinated in a typical octahedral fashion by two symmetry-related Me_2Vio^- ligands and two pairs of H_2O ligands. One of the latter is in a μ-bridging mode (O5), while the other is coordinated terminally to sodium (O6). This connectivity pattern results in the formation of almost planar Na_2O_2 rings perpendicular to the dimethylviolurate's C_4N_2 plane, which are edge-linked into an infinite ladder structure (Figure 5). Both Na–O4 distances are identical at 254.4(1) pm. Coordination of a $O{=}C(NR_2)_2$ fragment to sodium has been observed in various other compounds, e.g. in a barbituric acid derivative[36] and in a diazaphosphinanide.[37]

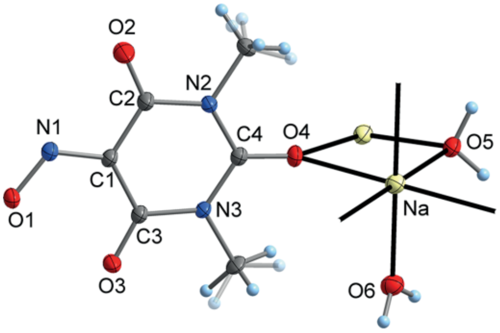


Figure 4. The asymmetric unit in the crystal structure of $Na(Me_2Vio)(H_2O)_3$ (**4a**), showing the atom numbering scheme and rotational disorder of the methyl groups. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level. The Na atom is located on a crystallographic center of inversion, and the Me_2Vio^- ligand and H_2O molecule O5 are situated on a mirror plane.

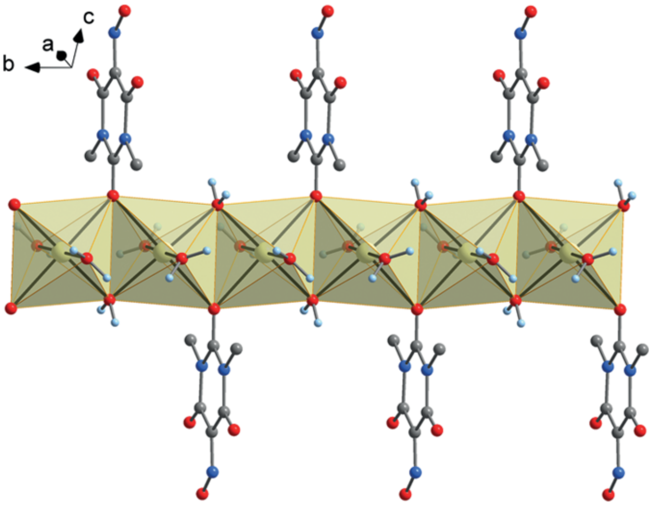


Figure 5. Interconnection of $Na(Me_2Vio)(H_2O)_3$ units in **4a** by μ-bridging Me_2Vio^- and H_2O ligands. The 1D-polymeric structure extends along the crystallographic *b* axis.

The solid-state structures of the dimethylviolurates of the heavier alkali metals K (**5**), Rb (**6**), and Cs (**7**) are more complex than those of their lighter homologs Li and Na. This is due to the less surprising finding that the M^+ ions adopt coordination numbers larger than six and Me_2Vio^- coordination dominates over hydration, resulting in close polymeric structures of dimensionalities larger than one. The potassium salt crystallized from aqueous medium as the hemihydrate $K(Me_2Vio)(H_2O)_{0,5}$ (**5**), which contains two $K(Me_2Vio)$ units and one equiv. H_2O in the asymmetric unit (Figure 6). Both potassium atoms exhibit an irregular seven-coordination by oxygen atoms, but the coordination modes of the two Me_2Vio^- units are different. One of them displays a tetradentate κ^2*O*,*O'*:κ*O*:κ*O''* mode, and for the other one the coordination is extended to heptadentate κ^2*O*,*O'*:κ*O*:κ*O*:κ*O'*:κ*O''*:κ*O''*. Since the carbonyl group in 2-position remains non-coordinated in both cases, the Me_2Vio coordination in **5** is more similar to that in **3** than to that in **4a**. The additional H_2O ligand in the potassium salt adopts an unusual μ_3-bridging coordination, thus resulting in a total of 14 different K–O bonds. These vary from 267.2(2) to 296.9(2) pm, which is within the typical range for potassium-oxygen compounds.[38] The result of the connectivity pattern in **5** is a close two-dimensional array (Figure 7).

The solid-state structure of the rubidium salt **6** shows some similarities to that of **5**, but the packing of the M^+ and Me_2Vio^- ions is much more symmetric. Different from the potassium derivative, the asymmetric unit of **6** contains only one formula unit $M(Me_2Vio)$ and no crystal water (Figure 8). However, the metal atom is again seven-coordinate in an irregular fashion, which is realized by involving all four oxygen donors (O1–O4)

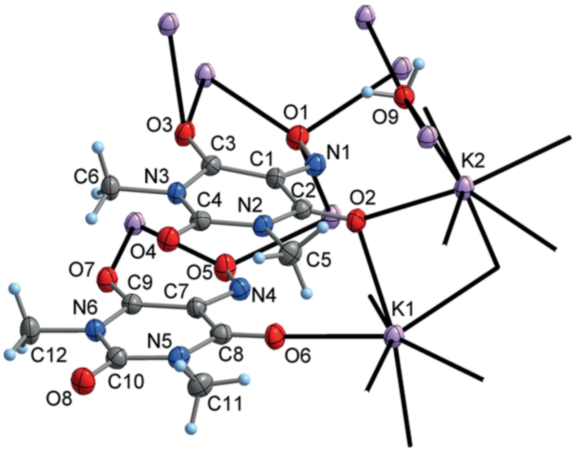


Figure 6. The asymmetric unit in the crystal structure of K(Me_2Vio)(H_2O)$_{0.5}$ (**5**), showing the atom numbering scheme. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

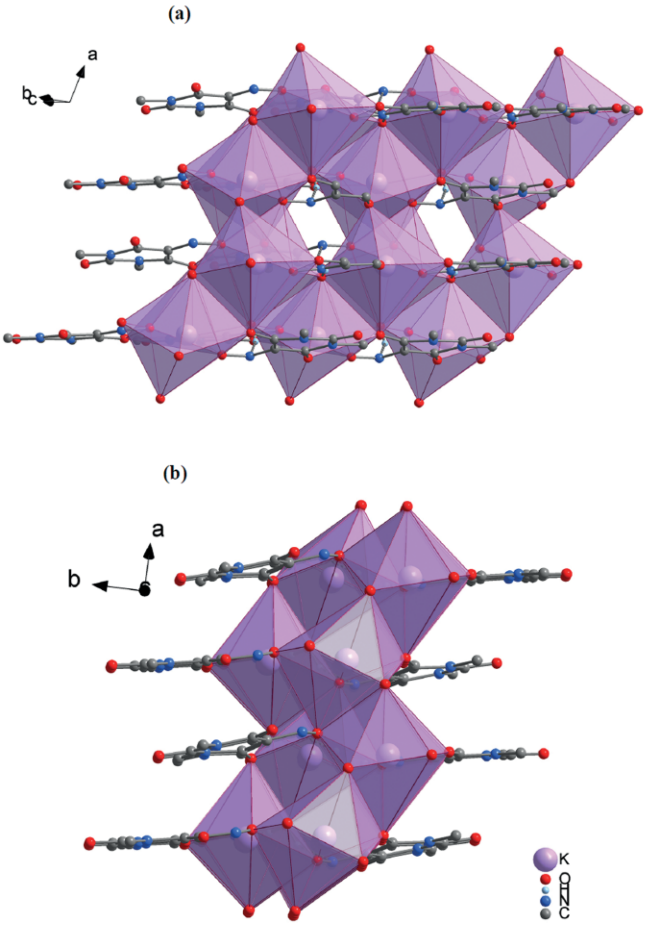


Figure 7. Illustration of the two-dimensional polymeric structure of **5** in the solid state, viewed in a projection on (a) and along (b) the layer. The layer extends parallel to (0 1 0).

as well as the nitroso nitrogen atom (N1). Similar as in the lightest alkali metal homolog **3**, the coordination pattern comprises both a six-membered chelate ring through κ^2O,O'-coordination and a five-membered chelate ring through κ^2N,O'-coordination. In both ring motifs, the Rb atom is almost perfectly in plane with the dimethylviolurate ligand. The Rb–O bond lengths range from 280.0(5) to 304.3(5) pm and are therefore typical for coordination compounds of rubidium, while the Rb-N contact is relatively long at 314.0(6) pm.[38] The increased number of metal-dimethylviolurate contacts in **6** as compared to **5** leads to the expansion of the polymeric structure into the third dimension, giving a closely packed 3D framework.

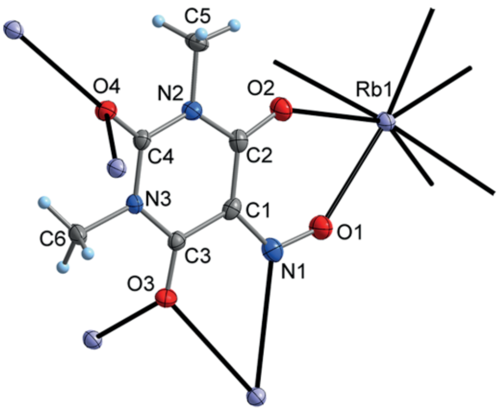


Figure 8. The asymmetric unit in the crystal structure of Rb(Me_2Vio) (**6**), showing the atom numbering scheme. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

The heaviest homolog of the alkali metal dimethylviolurate series, Cs(Me_2Vio) (**7**), crystallizes in anhydrous form, forming a solid-state structure which is less symmetric than that of **6**. The asymmetric unit contains two Cs^+ and two Me_2Vio^- ions, which exhibit different coordination environments (Figure 9). Both dimethylviolurate units form five- and six-membered chelate rings through κ^2O,O'- and κ^2N,O'-coordination, respectively. Similar as in **5** and different than in **6**, the carbonyl groups in 2-position of both Me_2Vio^- ions do not contribute to metal coordination. In their chelate rings, the cesium atoms are significantly displaced from the ligand plane, suggesting the presence of additional coordinative interactions with the dimethylviolurate's π-electron system. Consequently, the coordination around the cesium atoms is less clearly defined and makes the assignment of specific coordination numbers difficult. In spite of the close interconnection between Cs^+ and two Me_2Vio^- ions, the polymeric solid-state structure of **7** extends in only two dimensions.

Conclusions

In summarizing the results reported here, we synthesized a complete series of brightly colored alkali metal 1,3-dimethylviolurates. All new compounds were fully characterized by their IR and NMR (^1H, ^{13}C) spectra, elemental analyses, and single-crystal X-ray diffraction. All compounds exhibit polymeric structures in the solid state, which range from one- (Li, Na) over two- (K, Cs) to three-dimensional (Rb). The metal coordination follows the typical rules for the alkali metal series, with increasing coordination numbers in going from Li

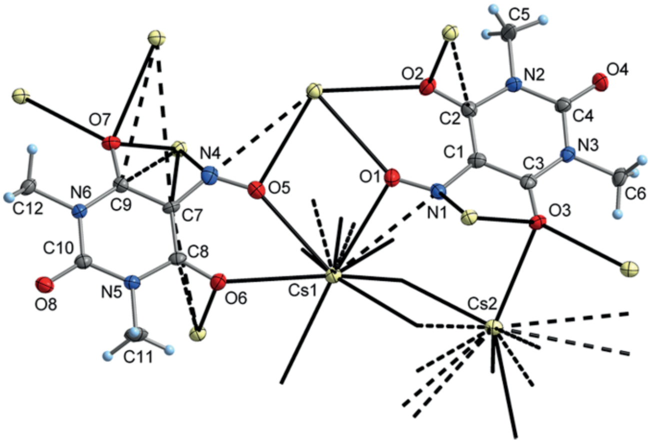


Figure 9. The asymmetric unit in the crystal structure of Cs(Me_2Vio) (**7**), showing the atom numbering scheme. Displacement ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

(five) to Na (six) to K and Rb (seven). Cesium shows a less defined coordination by additional π-coordinative interactions, which is also typical for the heavier alkali metals.[39] Also typical for the alkali metals is that the crystal water content in the isolated products decreased in the direction Li → Cs, which can be attributed to the fact that ionic binding becomes more and more relevant in the same direction. Regarding the coordination of the Me_2Vio^- ligand, $\kappa^2 O,O'$- and $\kappa^2 N,O'$-chelating modes, which have been frequently seen also with other metals, turned out to be the most favored coordination patterns. However, the sodium derivative Na(Me_2Vio)(H_2O)$_2$ represents a remarkable exception, as the Me_2Vio^- ligand is attached to the metal atom exclusively by the 2-carbonyl group in a monodentate mode. In the other alkali metal derivatives, the 2-carbonyl group often remains non-coordinated, which might be for steric reasons, as this group is most efficiently shielded by two methyl groups.

Experimental Section

General Methods: All operations were performed under atmospheric conditions without exclusion of air. The starting materials 1,3-dimethylbarbituric acid and MOH (M = Li–Cs) were obtained from commercial sources and used as received. 1,3-dimethylvioluric acid (= HMe_2Vio; **2**) was prepared according to the literature procedure.[27] ^{1}H and ^{13}C NMR spectra were recorded in D_2O solutions on a Bruker-Biospin AVIII 400 MHz spectrometer at 25 °C. Chemical shifts are referenced to tetramethylsilane. IR spectra were measured with a Bruker-Optics VERTEX 70v spectrometer equipped with a diamond ATR unit between 4000 cm^{-1} and 400 cm^{-1}. Microanalysis (C, H, N) of the compounds were performed using a "vario EL cube" apparatus from Elementar Analysensysteme GmbH. Melting / decomposition points were measured on a Büchi Melting Point B-540 apparatus.

X-ray Crystal Structure Analyses: Single crystal X-ray intensity data of the compounds reported in this paper were collected on a STOE IPDS 2T diffractometer equipped with a 34 cm image plate detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved with SHELXT-2018/3[40] and refined by full-matrix least-squares methods on F^2 using SHELXL-2016/4,[41] using the Olex 1.2 environment.[42]

Li(Me_2Vio)(H_2O) (3): 2.03 g (10.0 mmol) H(Me_2Vio)(H_2O) (**2**) dissolved in ca. 50 mL of hot ethanol (96 %) were added to a solution of 0.24 g (10.0 mmol) LiOH in 50 mL hot ethanol. Immediately the color of the solution turned to red. Compound **3** crystallized as orange-red prisms after standing for 5 d at 20 °C. Yield: 1.4 g (67 %). Mp. 185 °C (dec.). $C_6H_8LiN_3O_5$ (M = 209.09): calcd. C 34.47, H 3.86, N 20.10; found: C 34.36, H 3.95, N 19.81 %. **^{1}H NMR** (400.1 MHz, D_2O, 20 °C): δ = 3.18 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3) ppm. **^{13}C NMR** (100.6 MHz, D_2O, 21 °C): δ = 164.7 (NN*C*=O), 152.9 (*C*=O), 152.4 (*C*=O), 143.0 (*C*=N), 27.9 (CH_3), 26.8 (CH_3) ppm. **^{7}Li NMR** (155.5 MHz, D_2O, 21 °C): δ = –0.01 ppm. **IR** (ATR): ṽ = 3490 m ν(H_2O), 2962 w ν(C–H), 1720 m ν(C=O), 1613 vs. ν(C=O), 1463 s ν(N=O) cm^{-1}.

Na(Me_2Vio)(H_2O) (4): 2.03 g (10.0 mmol) H(Me_2Vio)(H_2O) dissolved in ca. 50 mL ethanol (96 %) at 50 °C were added to a solution of 0.42 g (10.5 mmol) NaOH in 75 mL hot ethanol. Immediately the color of the solution turned to red-pink. [Na(Me_2Vio)(H_2O)] precipitated as very fine pink needles. The solid was filtered of, washed with ethanol and dried at room temperature. Yield: 1.8 g (80 %). Mp. 153 °C (dec.). $C_6H_8N_3NaO_5$ (M = 225.14): calcd. C 32.01, H 3.58, N 18.66; found: C 31.96, H 3.43, N 19.05 %. **^{1}H NMR** (400.1 MHz, D_2O, 20 °C): δ = 4.70 (s, 2 H, H_2O), 3.24 (s, 3 H, CH_3), 3.08 (s, 3 H, CH_3) ppm. **^{13}C NMR** (100.6 MHz, D_2O, 21 °C): δ = 165.4 (NN*C*=O), 153.0 (*C*=O), 152.8 (*C*=O), 143.0 (*C*=N), 27.9 (CH_3), 26.7 (CH_3) ppm. **IR** (ATR): ṽ = 3557 m ν(H_2O), 3512 m ν(H_2O), 2970 w ν(C–H), 1715 m ν(C=O), 1654 vs. ν(C=O), 1618 vs. ν(C=O), 1465 s ν(N=O) cm^{-1}. Single-crystals of the monohydrate **4** could not be obtained. Recrystallization from **4** hot water afforded the known trihydrate Na(Me_2Vio)(H_2O)$_3$ (**4a**).[26] The purple crystals of **4a** were suitable for single-crystal X-ray structure determination.

K(Me_2Vio)(H_2O)$_{0.5}$ (5): 2.03 g (10.0 mmol) H(Me_2Vio)(H_2O) (**2**) dissolved in ca. 50 mL ethanol (96 %) at an temperature of 50 °C were added to a solution of 0.60 g (10.7 mmol) KOH in 75 mL hot ethanol. Immediately the color of the solution turned to purple, and compound **5** precipitated as a blue solid. The solid was isolated by filtration, washed with ethanol and dried at room temperature. Blue-violet crystal plates of **5** were formed in the mother liquor after standing for 5 days at 20 °C. Yield: 2.1 g (90 %). Mp. 245 °C (dec.). $C_{12}H_{14}K_2N_6O_9$ (M = 464.47): calcd. C 31.03, H 3.04, N 18.09; found: C 30.86, H 3.23, N 17.81 %. **^{1}H NMR** (400.1 MHz, D_2O, 20 °C): δ = 4.70 (s, H_2O), 3.19 (s, 3 H, CH_3), 3.02 (s, 3 H, CH_3) ppm. **^{13}C NMR** (100.6 MHz, D_2O, 21 °C): δ = 167.4 (NN*C*=O), 154.9 (*C*=O), 154.7 (*C*=O), 146.0 (*C*=N), 30.1 (CH_3), 28.9 (CH_3) ppm. **IR** (ATR): ṽ = 3479 m ν(H_2O), 2966 w ν(C–H), 1718 m ν(C=O), 1709 m ν(C=O), 1634 vs. ν(C=O), 1466 s ν(N=O) cm^{-1}.

Rb(Me_2Vio) (6): 2.03 g (10.0 mmol) H(Me_2Vio)(H_2O) (**2**), dissolved in ca. 50 mL ethanol (96 %) at 50 °C, were added to a solution of 1.50 g (10.8 mmol) RbOH·2H_2O in 75 mL hot ethanol. Immediately the color of the solution turned to purple, and 5 precipitated as blue solid. The solid was filtered off, washed with ethanol and dried at room temp. Blue, needle-like crystals of **6** were formed in the mother liquor after standing for 3 days at 20 °C. Yield: 2.0 g (74 %). Mp. 272 °C (dec.). $C_6H_6N_3O_4Rb$ (M = 269.60): calcd. C 26.73, H 2.24, N 15.59; found: C 26.66, H 2.29, N 15.41 %. **^{1}H NMR** (400.1 MHz, D_2O, 20 °C): δ = 4.73 (s, H_2O), 3.17 (s, 3 H, CH_3), 3.00 (s, 3 H, CH_3) ppm. **^{13}C NMR** (100.6 MHz, D_2O, 21 °C): δ = 167.3 (NN*C*=O), 154.7 (*C*=O), 154.6 (*C*=O), 146.0 (*C*=N), 30.1 (CH_3), 28.9 (CH_3) ppm. **IR** (ATR): ṽ = 3325 m ν(H_2O), 2965 w ν(C–H), 1717 m ν(C=O), 1632 vs. ν(C=O), 1464 m ν(N=O) cm^{-1}.

Cs(Me_2Vio) (7): 2.03 g (10.0 mmol) H(Me_2Vio)(H_2O) (**2**) dissolved in ca. 50 mL ethanol (96 %) at 50 °C were added to a solution of 2.00 g

(10.7 mmol) $CsOH{\cdot}2H_2O$ in 75 mL hot ethanol. Immediately the color of the solution turned to purple. Compound **7** precipitated as blue solid. The solid was filtered off, washed with ethanol and dried at room temp. Blue, needle-like single-crystals of **7** were formed in the mother liquor after standing for one week at 20 °C. Yield: 2.5 g (79 %). Mp. 266 °C (dec.). $C_6H_6N_3O_4Cs$ (M = 317.04): calcd. C 22.73, H 1.91, N 13.25; found: C 22.27, H 2.15, N 13.51 %. **^{1}H NMR** (400.1 MHz, D_2O, 20 °C): $\delta = 4.73$ (s, H_2O), 3.11 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3) ppm. **^{13}C NMR** (100.6 MHz, D_2O, 21 °C): $\delta = 167.1$ (NN*C*=O), 154.4 (*C*=O), 154.3 (*C*=O), 145.9 (*C*=N), 30.1 (*C*H$_3$), 28.9 (*C*H$_3$) ppm. **^{133}Cs NMR** (52.5 MHz, D_2O, 21 °C): $\delta = 3.52$ ppm. **IR** (ATR): $\tilde{\nu} = 2955$ w ν(C–H), 1706 m ν(C=O), 1617 vs. ν(C=O), 1470 m ν(N=O) (m) cm^{-1}.

Crystallographic data (including structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2026755 (**3**), CCDC-1865463 (**4a**), CCDC-2026756 (**5**), CCDC-2026757 (**6**), and CCDC-2026758 (**7**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): IR and NMR spectra of all title compounds.

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