Supporting information (SI)

Metal salts of the binary 4,5-dicyano-2*H*-1,2,3-triazole anion ($[C_4N_5]^-$)

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Table 1 Calculated (scaled) and measured IR and Raman frequencies with intensity (IR) and activity (Raman) values for the 4,5-dicyano-2*H*-1,2,3-triazole anion (ν > 250 cm^{-1}).

	ν_{scal} (cm^{-1})[a]	I_{calc}/ A_{calc} IR/Raman[b]	ν_{meas} (IR, cm^{-1})[c]	ν_{meas} (Raman, cm^{-1})[d]	Mode Assignment[e]
1	473	0/3	460(w)	430(5)	γ(N–N–C)$_{ring}$ + γ(C–C≡N)
2	475	1/3	475(w)	470(5)	δ(C–C≡N)
3	506	3/4		500(2)	ν(C–C) + δ(N–C–C)$_{ring}$
4	537	6/3	520(m)	525(10)	γ(C–C≡N)
5	619	4/0	605(w)		δ(C–C≡N)
6	629	2/14	630(w)		ν(C–C)
7	652	0/2	650(vw)	655(2)	γ(N–C–C)$_{ring}$
8	687	0/0	710(vw)	710(2)	γ(N_3)
9	970	0/6	1000(vw)	1010(10)	δ(N_3)
10	1052	3/50	1090(w)	1090(10)	ν(N–N)
11	1145	36/0	1165(m)		ν(C–N)$_{ring}$
12	1149	10/4	1180(m)	1160(2)	ν(N–N)
13	1241	4/19	1280(w)	1290(10)	ν_s(C–N)$_{ring}$
14	1330	50/35	1365(m)	1375(10)	ν_{as}(C–N)$_{ring}$
15	1445	13/90	1500(w)	1505(20)	ν(C–C)$_{ring}$
16	2219	175/319	2240(s)	2240(70)	ν_{as}(C≡N)
17	2223	144/519	2250(s)	2250(100)	ν_s(C≡N)

[a] Calculated frequencies (B3LYP/6-311+G(d,p))[1,2] scaled by 0.9613;[3] [b] Calculated IR intensities and Raman activities; [c] Experimental IR frequencies and intensities; [d] Experimental Raman frequencies and activities in () brackets; [e] Approximate description of vibrational modes: ν = stretching, δ = in-plane bending, γ = out-of-plane bending, ω = in-plane rocking, τ = torsion; as = asymmetric and s = symmetric.

Table 2 Selected distances (Å) and angles (°) for the coordination around the Rb^{+} cation in compound **4**.

Rb–N5	3.028(3)	Rb–N4^{iii}	3.065(3)
Rb–N6	2.938(3)	Rb–N1^{iv}	3.271(3)
Rb–N1^{i}	3.062(3)	Rb–N9^{v}	3.168(3)
Rb–N4^{ii}	3.124(3)	Rb–N9^{vi}	3.017(3)
Rb–N5^{ii}	3.166(3)		
N1–Rb–N4^{ii}	66.9(1)	N5^{ii}–Rb–N1^{iv}	122.2(1)
N1–Rb–N5^{ii}	91.4(1)	N5^{ii}–Rb–N9^{v}	155.2(1)
N1–Rb–N4^{iii}	75.5(1)	N5^{ii}–Rb–N9^{vi}	109.8(1)
N1–Rb–N1^{iv}	110.6(1)	N4^{iii}–Rb–N5	100.3(1)
N1–Rb–N9^{v}	64.7(1)	N4^{iii}–Rb–N6	124.4(1)
N1–Rb–N9^{vi}	69.8(1)	N4^{iii}–Rb–N1^{iv}	65.0(1)
N1–Rb–N5	170.4(1)	N4^{iii}–Rb–N9^{v}	155.2(1)
N1–Rb–N6	160.0(1)	N4^{iii}–Rb–N9^{vi}	109.8(1)
N4^{ii}–Rb–N5^{ii}	24.6(1)	N5–Rb–N6	25.8(1)
N4^{ii}–Rb–N4^{iii}	68.1(1)	N5–Rb–N1^{iv}	74.5(1)
N4^{ii}–Rb–N5	103.6(1)	N5–Rb–N9^{v}	124.7(1)
N4^{ii}–Rb–N6	118.5(1)	N5–Rb–N9^{vi}	114.0(1)
N4^{ii}–Rb–N1^{iv}	131.7(1)	N6–Rb–N1^{iv}	80.7(1)
N4^{ii}–Rb–N9^{v}	131.4(1)	N6–Rb–N9^{v}	108.5(1)
N4^{ii}–Rb–N9^{vi}	97.7(1)	N6–Rb–N9^{vi}	90.3(1)
N5^{ii}–Rb–N4^{iii}	70.6(1)	N1^{iv}–Rb–N9^{v}	65.4(1)
N5^{ii}–Rb–N5	79.0(1)	N1^{iv}–Rb–N9^{vi}	127.8(1)
N5^{ii}–Rb–N6	96.2(1)	N9^{v}–Rb–N9^{vi}	69.5(1)

Symmetry codes: (i) x, –1+y, z; (ii) 2–x, 1–y, 1–z; (iii) 2–x, –0.5+y, 1.5–z; (iv) x, 1.5–y, 0.5+z; (v) 1–x, 1–y, 1–z; (vi) 1–x, –0.5+y, 0.5–z.

Table 3 Selected distances (Å) and angles (°) for the coordination around the Mg^{2+} cation in compound **6**.

Mg–O10	2.046(3)	Mg–O10^{i}	2.046(3)
Mg–O11	2.065(3)	Mg–O12^{i}	2.056(3)
Mg–O12	2.056(3)	Mg–O11^{i}	2.065(3)
O10^{i}–Mg–O12^{i}	90.5(1)	O11^{i}–Mg–O11	179.9(1)
O10^{i}–Mg–O11^{i}	89.7(1)	O10–Mg–O11	89.7(11)
O12^{i}–Mg–O11^{i}	90.2(1)	O10^{i}–Mg–O12	89.4(11)
O10^{i}–Mg–O10	179.9(1)	O12^{i}–Mg–O12	179.9(1)
O12^{i}–Mg–O10	89.4(1)	O11^{i}–Mg–O12	89.7(1)
O11^{i}–Mg–O10	90.2(1)	O10–Mg–O12	90.5(1)
O10^{i}–Mg–O11	90.2(1)	O11–Mg–O12	90.2(1)
O12^{i}–Mg–O11	89.7(1)		

Symmetry codes: (i) 2–x, 1–y, 2–z; (ii) 1+x, 1.5–y, 0.5+z.

Table 4 Selected distances (Å) and angles (°) for the coordination around the Sr^{2+} cation in compound **8b**.

Sr–N23^{i}	2.726(4)	Sr–O13	2.709(3)
Sr–O13^{i}	2.726(3)	Sr–O14	2.476(4)
Sr–O2	2.538(3)	Sr–O24	2.581(4)
Sr–O12	2.552(3)	Sr–O25	2.545(4)
N23^{i}–Sr–O13^{i}	71.0(1)	O13–Sr–O14	69.2(1)
N23^{i}–Sr–O2	133.0(1)	N23^{i}–Sr–O24	70.1(1)
O13^{i}–Sr–O2	140.8(1)	O13^{i}–Sr–O24	93.8(1)
N23^{i}–Sr–O12	125.2(1)	O2–Sr–O24	73.7(1)
O13^{i}–Sr–O12	71.5(1)	O12–Sr–O24	74.1(1)
O2–Sr–O12	69.4(1)	O13–Sr–O24	140.3(1)
N23^{i}–Sr–O13	70.3(1)	N23^{i}–Sr–O25	72.9(1)
O13^{i}–Sr–O13	70.2(1)	O13^{i}–Sr–O25	140.9(1)
O2–Sr–O13	140.2(1)	O2–Sr–O25	76.8(1)
O12–Sr–O13	128.8(1)	O12–Sr–O25	145.0(1)
N23^{i}–Sr–O14	138.8(1)	O13–Sr–O25	83.7(1)
O13^{i}–Sr–O14	102.1(1)	O14–Sr–O24	150.3(1)
O2–Sr–O14	78.1(1)	O14–Sr–O25	94.8(1)
O12–Sr–O14	87.2(1)	O24–Sr–O25	88.0(1)

Symmetry code: (i) 1–x, 1–y, 1–z.

Table 5 Selected hydrogen-bonding geometry for compounds **6** and **8b**

D–H•••A^{b}	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (º)
		6		
O10–H102•••N6^{i}	0.827(4)	2.042(4)	2.857(1)	171.0(2)
O10–H101•••N1^{ii}	0.841(4)	2.053(4)	2.886(1)	175.1(2)
O11–H112•••O13	0.819(4)	1.973(4)	2.762(1)	167.0(2)
O11–H111•••N9^{iii}	0.836(4)	2.230(5)	2.944(1)	144.8(2)
O12–H122•••O13^{iv}	0.838(4)	2.008(4)	2.824(1)	174.9(1)
O12–H121•••N4	0.838(4)	2.005(5)	2.796(1)	160.1(2)
O13–H131•••N5	0.852(4)	1.958(4)	2.775(1)	163.4(2)
		8b		
O23–H231•••N14^{i}	0.829(4)	1.991(4)	2.814(1)	171.9(2)
O21–H212•••N15^{ii}	0.833(4)	2.528(4)	3.107(1)	127.6(1)
O21–H212•••N16^{ii}	0.833(3)	2.002(4)	2.796(1)	158.7(1)
O21–H211•••N4^{iii}	0.831(4)	2.498(5)	3.265(1)	153.8(1)
O22–H222•••N15^{iv}	0.822(3)	2.024(4)	2.845(1)	176.1(1)
O9–H91•••N4^{v}	0.854(4)	2.317(5)	3.168(1)	174.4(1)
O22–H221•••N15^{vi}	0.816(4)	2.424(4)	3.154(1)	149.5(1)
O24–H242•••N5^{v}	0.823(4)	2.058(4)	2.870(1)	169.2(2)

Symmetry codes for **6**: (i) x, 1.5–y, 0.5+z; (ii) 1–x, 1–y, 2–z; (iii) 1+x, 1.5–y, 0.5+z; (iv) 2–x, 1–y, 1–z. **8b**: (i) 0.5–x, –0.5+y, 1.5–z; (ii) –0.5+x, 1.5–y, –0.5+z; (iii) –0.5+x, 1.5–y, 0.5+z; (iv) 1.5–x, –0.5+y, 1.5–z; (v) 0.5+x, 1.5–y, 0.5+z; (vi) 0.5+x, 1.5–y, –0.5+z.

Graph-set discussion of compounds 6 and 8b

Using the formalism of graph-set analysis,[4,5] the seven hydrogen bonds found in the structure of **6** form **D1,1(2)** dimmeric graph-sets and six of these hydrogen bonds also form dimmeric **D2,2(7)** interactions (primary level). At the secondary level, finite **D2,2(X)** (X = 4, 5, 7) and infinite **C1,2(6)** and **C2,2(X)** (X = 8–11) chain patterns and ring hydrogen-bonded networks of the type **R2,4(12)** and **R4,4(18)** can be found. Fig. 1a shows a view of the smaller **R2,4(12)** patterns, which are formed by interaction of the magnesium octahedrons over water molecules (O11•••O13 = 2.762(1) and O12•••O13^{iv} = 2.824(1) Å; symmetry code: (iv) 2–x, 1–y, 1–z). These patterns form infinite **C1,2(6)** chains along the *c*-axis. Fig. 1b shows the larger **R4,4(18)** graph-sets, which are formed by interaction of the magnesium octahedrons over anions (O10•••N1^{ii} = 2.886(1) and O11•••N9^{iii} = 2.944(1) Å; symmetry codes: (ii) 1–x, 1–y, 2–z; (iii) 1+x, 1.5–y, 0.5+z). In analogy to the **R2,4(12)** patterns described above, these graph-sets also form infinite chains, which run parallel to the *a*-axis and take the graph-set descriptor **C2,2(9)**.

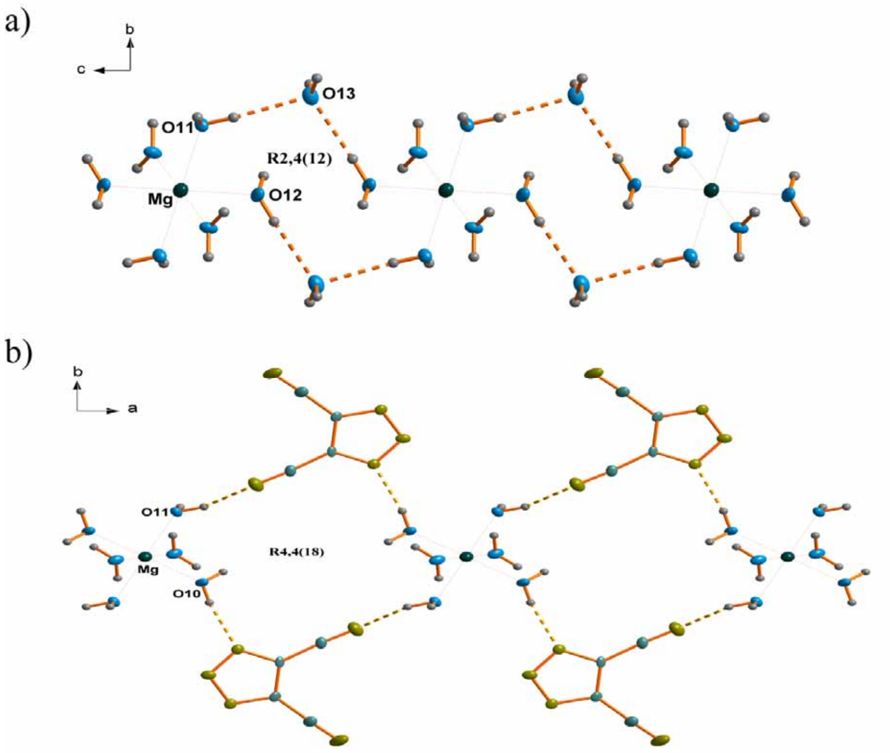

Fig. 1 Ring hydrogen-bonding graph-sets in the crystal structure of compound **6** (a) view along the *a*-axis and b) view along the *c*-axis. Thin lines represent coordination around the Mg^{2+} cations and thick dotted lines represent hydrogen bonds.

The structure of compound **8b** shows extensive hydrogen-bonding (Table 5). Using the formalism of graph-set analysis, the eight hydrogen bonds found in the structure of the compound form seven **D1,1(2)** dimmeric graph-sets and one **C1,1(6)** infinite chain (primary level). This later motif is the only chain hydrogen-bonding motif found in the structure and is formed by the interaction of the carboxylic acid proton of one anion with one of the triazole ring nitrogen atoms (O9•••N4^{v} = 3.168(1) Å, symmetry code: (v) 0.5+x, 1.5–y, 0.5+z). At the secondary level, most of the graph-sets formed are dimmeric interactions, which take the labels **D1,2(2)**, **D2,1(3)**, **D2,3(9)**, **D2,2(X)** (X = 4, 5, 7) and **D3,3(X)** (X = 10, 11). Additionally, ring hydrogen-bonded networks with the descriptors **R2,1(3)** and **R2,4(8)** are also found. The first are formed by the side-on interaction of two nitrogen atoms of a triazole anion with a water molecule (O21•••N16^{ii} = 2.796(1) Å and O21•••N15^{ii} = 3.107(1) Å; symmetry code: (ii) –0.5+x, 1.5–y, –0.5+z) and the latter by the hydrogen bonds formed by two molecules of water (O22•••N15^{iv} = 2.845(1) Å and O22•••N15^{vi} = 3.154(1) Å; symmetry codes: (iv) 1.5–x, –0.5+y, 1.5–z; (vi) 0.5+x, 1.5–y, –0.5+z) that bridge two triazole anions (Fig. 2).

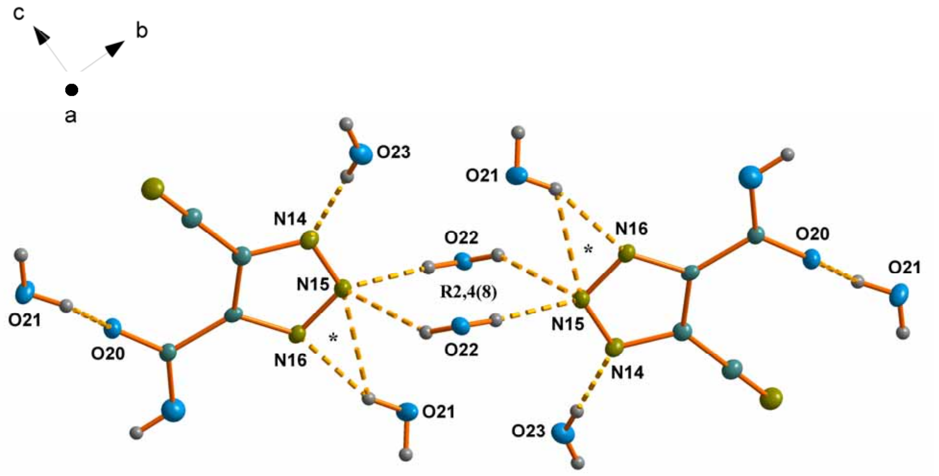

Fig. 2 Ring hydrogen-bonding graph-sets in the crystal structure of compound **8b.** The Sr^{2+} cations have been omitted for the sake of simplicity. * depict **R2,1(3)** graph sets and the thick dotted lines represent hydrogen bonds.

General method

All chemical reagents and solvents of analytical grade were obtrained from Sigma-Aldrich Inc. or Acros Organics and used as supplied. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Eclipse 400 instrument. The chemical shifts are given relative to tetramethylsilane as a external standard. Infrared (IR) spectra were recorded at room temperature on a Perkin-Elmer

Spectrum instrument equipped with a Universal ATR sampling accessory. Raman spectra were recorded on a Perkin-Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). IR intensities are given in parentheses as w = weak, m = medium and s = strong. Raman activities are reported in percentages relative to the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch Simultanous Thermal Analyzer STA 429. The thermal behavior was analyzed by differential scanning calorimetry (SETARAM DSC131 instrument, calibrated with standard pure indium and zinc) at a heating rate of $\beta = 5$ °C min^{-1} in closed aluminum containers and with a nitrogen flow of 20 mL min^{-1}. The reference sample was a closed aluminum container.

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