Two red salts derived from yellow 4-cyano-1-methylpyridinium iodide:
1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium triiodide and
4-cyano-1-methylpyridinium triiodide

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ABSTRACT

Crystal structures of 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium triiodide (m.p. 383°C) and 4-cyano-1-methylpyridinium triiodide (m.p. 118°C) are described. These red salts were obtained unexpectedly from yellow 4-cyano-1-methylpyridinium iodide in either water or methanol solution in contact with insoluble heavy metal chlorides under ambient conditions. Neither compound is widely described in the chemical literature.

INTRODUCTION

Numerous reports of host/guest compounds, metalloprisms or cages incorporate 2,4,6-tris(4-pyridyl)-1,3,5-triazine (usually abbreviated tpt or 4-tpt) as panels in large hexavalent [1-3] or dodecavalent [4] cations. Therrien [5] reviewed the coordination chemistry of 2,4,6-tri(pyridyl)-1,3,5-triazine ligands and Mooibroek and Gamez [6] discussed in detail all the numerous possible s-triazine supramolecular interactions. One of the crystal structures described herein contains a trivalent cation of 4-tpt methylated at the pyridine nitrogens. This new structure will contribute to our understanding of the non-covalent interactions in previously reported, as well as yet undiscovered, compounds such as the cages and prisms containing tethered triazine panels. Shedding light on the very existence of this trivalent triazinium cation may spark new ideas for this synthon.

In addition, triazine syntheses can require extreme conditions including high temperatures and pressures, high concentrations of strong base or acid, and long reaction times [5,7]. The present study describes a cyclotrimerization product formed under mild reaction conditions. Despite Kosower [8] and others having used and studied 4-cyano-1-methylpyridinium iodide and closely related compounds extensively, there are no published reports of the formation of either of the other two title compounds from that starting material.

In acidic aqueous solutions of 4-cyano-1-methylpyridinium iodide under ambient conditions in contact with insoluble heavy metal chloride solids, an electron transfer reaction takes place to form red 4-cyano-1-methylpyridinium triiodide, containing the linear triatomic anion (Compound I). In methanol, cyclotrimerization yields 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium triiodide with three monatomic

anions per trivalent cation (Compound II). Neither of these compounds has been widely discussed in the chemical literature. They have potential applications in photoelectrochemistry and supramolecular design. Methods of preparation, crystal structures, supramolecular features and other characteristics of these compounds are described herein.

Compound I

4-cyano-1-methylpyridinium triiodide

Compound II

1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyridinium triiodide

EXPERIMENTAL

All solvents and reagents were purchased from commercial suppliers and used without modifications. NMR spectrum was obtained with a Varian 400 MHz NMR. Melting points were obtained using a Shimadzu DSC-60 plus differential scanning calorimeter. Crystal structures were determined using a Bruker Smart APEX CCD single crystal X-ray diffractometer.

Synthesis of 4-cyano-1-methylpyridinium triiodide

0.5 g (2.0 mmol) of previously synthesized 4-cyano-1-methylpyridinium iodide [9] was dissolved in 20 mL of deionized water and acidified with three drops of 37% HCl(aq) to avoid hydrolysis of the nitrile group. A 2.2 mmol Cl⁻ equivalent of AgCl, Hg₂Cl₂ or PbCl₂ was added and the mixture was gently heated and stirred for 20 minutes. The cooled mixture was vacuum filtered and the precipitate discarded. The supernatant was filtered again via syringe and a 0.2 micron disc then covered loosely with Parafilm and left in the fume hood. Three weeks later black flakes were collected by vacuum filtration, air dried and analyzed by single crystal X-ray diffraction. Yield 9%, n.m.pt. 118°C.

Original synthesis of 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyridinium trisiodide (mixed product)

0.26 g (1.1 mmol) of previously synthesized 4-cyano-1-methylpyridinium iodide [9] was readily dissolved in 10 mL of methanol. The yellow solution turned brownish over time. 0.29 g of Hg₂Cl₂ (1.2 mmol Cl⁻) was added and the mixture was stirred for 10 minutes, becoming almost black. The mixture was vacuum filtered and the olive precipitate was washed with a few mL of methanol and then discarded. The clear pomegranate-colored supernatant was left to evaporate in the fume hood. The same steps were carried out with 0.25 g 4-cyano-1-methylpyridinium iodide and 0.17 g PbCl₂ (1.2 mmol Cl⁻) producing a dark brown mixture that separated into a yellowish precipitate and an amber colored supernatant. AgCl was not used in this reaction. The solid product from evaporation of both supernatants appeared brick red and was found by optical microscopy to consist of clumps of red needles grown on top of clear plates. The crystal structure of the clear plates showed them to be 4-carbamido-1-methylpyridinium iodide while the red needles were found to be 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyridinium trisiodide.

Alternative synthesis of 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyridinium trisiodide

Commercially available 2,4,6-tris-(4-pyridyl)-1,3,5-triazine (0.75 g, 2.4 mmol) was mixed with 20 mL of dimethylformamide (DMF) and briefly stirred until opaque. Methyl iodide (0.60 mL, 9.6 mmol) was added via glass syringe. The mixture turned red after 10 minutes of heating at 90°C and was then allowed to stir for 48 h at 90°C with reflux. The resulting red solid was collected via vacuum filtration and washed with 6 mL of diethyl ether. The dried solid was recrystallized from hot water. After slow cooling, vacuum filtration, cold water wash and air drying, 1.7 g of dark, shiny needles was obtained. This product showed two melting point peaks at 343°C and 383°C. To purify, 1.4 g was dissolved in 20 mL of hot water and then cooled slowly. After about 1 hour, this orange

solution produced long dark needles with a yellow supernatant. Vacuum filtration, cold water wash and air drying gave long shiny dark red needles (1.14 g, 81% recovery, 65% overall yield, n.m.pt. 383°C). Slow evaporation of the combined filtrate and wash eventually grew additional needles several cm long. The NMR of the recrystallized product coincides with that reported by Gries et al. [10] for the hexafluorophosphate salt of the same triazinium cation. ¹H-NMR (400 MHz, [D₆] DMSO) δ = 9.48 (d, 6H, 2-H, 2'-H, 2''-H, 6-H, 6'-H, 6''-H), 9.36 (d, 6H, 3-H, 3'-H, 3''-H, 5-H, 5'-H, 5''-H), 4.50 (s, 9H, 1-H, 13'-H, 13''-H)

X-ray Crystallography

Crystals of **I** and **II** were mounted on Mitegen loops with a drop of Paratone oil and placed in a cold nitrogen stream on the Bruker Smart APEX diffractometer. Full spheres of data were collected under control of the APEX2 program suite [11] with data treatment, structure solution and refinement performed as described elsewhere [12]. Relevant crystallographic data are listed in Table 1.

RESULTS AND DISCUSSION

Compound I

Several salts of the 4-cyano-1-methylpyridinium cation have been produced readily by salt metathesis (double displacement) between the 4-cyano-1-methylpyridinium iodide and more soluble silver salts containing the desired anion [13]. However, we were unable to generate 4-cyano-1-methylpyridinium chloride by this method. Instead, crystals of the triiodide salt, **I**, were obtained when the reaction was done in acidic aqueous solution. Similar attempts using mercury(I) chloride and lead(II) chloride also produced **I** rather than the target 4-cyano-1-methylpyridinium chloride. Slow evaporation of the yellow filtrate from these reactions eventually yields apparently black flakes that are revealed to be blocky red crystals when examined with transmitted light under an optical microscope. These crystals are of good quality for single-crystal X-ray diffraction and are found to contain the original organic cation and the linear triiodide anion, **I**. Crystallographic data are given in Table 1 with selected distances and angles in Table 2 and the unit cell is shown in Figure 1 (also see additional figures in Supplementary Information). The authors have found no previous reports in the chemical literature for an isolated triiodide salt of 4-cyano-1-methylpyridinium cation.

The crystal packing of **I** is based on intersecting layers in which cations and anions alternate across the layer although the axis of the triiodide anion makes an angle of 4.7° with the plane of the cation. The interlayer separation is 276 pm and the angle of intersection is 70° . Hydrogen bond and other geometrical data are given in Table 2. The anion is nearly linear ($177.084(9)^\circ$) and slightly asymmetric (I-I distances 293.86(3) and 291.34(3) pm). This geometry is well within the usual range found by Svensson and Kloo [14] in their 2003 review of bonding in polyiodides. As can be seen in Table 2 and Figure S1 in Supplementary Information, each anion exhibits seven close contacts to five different cations (two are C...C contacts of 359.9(4) and 364.4(4) pm which is less than the sum of the van der Waals radii (372 pm)) while pairs of cations form hydrogen-bonded inversion dimers between the nitrile N and ring hydrogens H3/H5 (see Figure S2 in Supplementary Information). The nitrile N also has close contacts with methyl groups on other cations. Both the 4-cyano-1-methylpyridinium iodide and bromide salts contain similarly hydrogen-bonded cation networks as well as close contacts between ring hydrogens and anions [9,13]. A substructure search of the Cambridge Crystallographic Database found a total of 13 crystal structures containing the 4-cyano-1-methylpyridinium cation. None of the other compounds show supramolecular features or crystal packing strongly resembling that of **I**.

The triiodide anion is typically generated by dissolving neutral iodine molecules in a solution containing iodide anions, usually as an alkali metal salt [15]. In this work, the triiodide anion was generated in sufficient amounts to form **I** in our intended methathesis reactions between solid heavy metal chloride salts and 4-cyano-1-methylpyridinium iodide in acidified aqueous solution. (HCl(aq) was added to inhibit hydrolysis of the nitrile group [16].) No molecular iodine was added. We speculate that dissolved oxygen acted as the oxidizing agent as all procedures were performed under

ambient conditions with agitation by stirring and filtering. Since the electrochemical potential for reduction of dissolved aqueous oxygen in acidic solution is 1.23 V and that for the oxidation of iodide to triiodide is -0.536 V [17], the overall redox potential for Reaction I is favorable at about +0.7 V.

In addition, small particles of insoluble salts might provide catalytic surface sites. Careful experiments will be required to provide mechanistic details for this reaction.

Several other relevant examples of triiodide production in aqueous reactions where air and iodide were present but molecular iodine was initially absent are worth noting. Kosower reported visual detection of minor amounts of triiodide or iodine by the interaction of air with wet 1-methylpyridinium iodide [18]. Two recent hydrothermal syntheses also generated characterizable crystalline triiodides. The first is a phase related to effective operation of certain dye-sensitized solar cells, 4-tert-butylpyridinium triiodide–4-tert-butylpyridine (1/1), described by Hongshan He & Sykes [19-21]. The second, an interesting 2D coordination network of Cu(TMBP)I₃ (TMBP = 3,3',5,5'-tetramethyl-4,4'-bipyrazole) where triiodide acts as a cross-linking unit between Cu centers, was synthesized by Jun He et al. [22]. These authors state that the presence of air accounts for oxidation of iodide to produce the cross-linking triiodides.

Compound II

Subsequently, while still trying to use anion exchange to generate crystals of 4-cyano-1-methylpyridinium chloride, the same experiment was repeated using methanol as the solvent. Another red product was obtained but upon examination with an optical microscope, it was evident that this solid was composed of red needles, some grown in clumps attached to clear plates. The clear plates were determined by single crystal X-ray diffraction analysis to be 4-carbamido-1-methylpyridinium iodide, the undesired hydrolysis product [16]. Surprisingly, the red needles were found to be 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium trisiodide, **II**. Crystallographic data for **II** are given in Table 1 and selected distances and angles in Table 3. Figures 2-4 show cation pairs with and without anions, a side view of a column of alternating cation pairs with anions, and a view down the crystallographic *c* axis (see Supplementary Information for an image of the unit cell).

The trivalent triazininium cation [CAS 135973-20-5] of **II** [CAS 42517-85-1] is particularly interesting as it has been shown to display four different oxidation states, including a diradical, all with half-wave potentials between -0.28 and -1.46 V vs. Ag/AgCl in 0.1 M n-butylammonium tetrafluoroborate acetonitrile solution [10]. The iodide salt is also named as a herbicide in a patent [23] and more recently as a reagent for the manufacture of nitrogen-containing carbon alloys [24] but little other mention of this cation can be found in the literature [25].

anion inside the cage rather than a coronene guest molecule, only four of the six anions are close to pyridine nitrogens, leading to very different crystal packing [1].

In order to obtain both a definitive melting point determination and a clean NMR spectrum of the red product, separation of the clear plates and red needles was attempted by physical segregation under an optical microscope. While it was possible to effect some enrichment of one over the other, complete separation of such tiny crystals was not possible by hand. Chromatographic methods were also unsuccessful. So, in order to allow additional characterization of the pure compound, 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium trisiodide was synthesized by methylation of 2,4,6-tris(4-pyridyl)-1,3,5-triazine using methyl iodide in DMF (see alternative synthesis in the Experimental section). The structures of crystals grown from this reaction product matched those collected as described above. Both structures have been deposited with the CCDC (1430162,1430163).

Computational Analysis

Dispersion corrected density functional theory (DFT-D) calculations were carried out at the BLYP-D/def2-SVP level of theory [27] in order to elucidate some of the energetic aspects of the crystal structure of **II**. Inclusion of the empirical dispersion correction term is very important for these systems as stacking interactions involving aromatic rings or iodide are likely to be largely dependent on dispersion contributions. Here some calculations are made in gas-phase while others use the conductor-like screening model (COSMO) in order to approximate the effect of the crystal environment [28]. As the permittivity of these crystals is currently unknown, a dielectric constant of 4.0 was chosen as a generic value. In all calculations the positions of heavy (non-hydrogen) atoms are held fixed at the crystal structure geometry while hydrogen positions are optimized at the BLYP-D/def2-SVP level of theory.

Interestingly, both gas-phase and implicit solvation (COSMO) calculations indicate that a flat structure for the 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium cation of **II** is more stable than the bowl configuration that is adopted in the crystal with energy differences of 9.1 kcal/mol (38 kJ/mol) for the gas-phase calculation and 7.2 kcal/mol (30 kJ/mol) using COSMO. This relatively large stability difference indicates that the non-covalent interactions of these cations with the surrounding iodides, and with each other, have a marked impact on the overall crystal structure.

Not surprisingly, implicit solvation interaction energies computed for both the concave (bottom-facing, interior iodides) and convex (bowed out, exterior iodides) pairs of cations (Figure 2) indicate repulsive interactions, with values of +118.7 kcal/mol (496.6 kJ/mol) and +138.0 kcal/mol (577.4 kJ/mol), respectively. Recall that the triazine ring centroids of the concave cation pairs are 31 pm farther away from each other than in the convex pairs (Table 3). Introduction of the six iodides most closely associated with each cation pair (Figure 2) results in strongly attractive interactions for both “octamer” (two cations plus six anions) types. Octamer binding energies as calculated using

Equation 1 for the concave (interior iodides) and convex (exterior iodides) structures are computed to be -298.0 kcal/mol (-1247 kJ/mol) and -295.0 kcal/mol (-1234 kJ/mol) respectively.

$$IE = E(\text{tot}) - 2E(\text{trivalent cation}) - 6E(\text{I}^-) \quad \text{Equation 1}$$

It is remarkable that these two octamers, whose structures are related but quite different, exhibit almost identical amounts of stabilization. This similarity in the stabilities of the concave and convex forms may help explain the coexistence of these two structures within the crystal framework. If either of the octamers were to have a stability significantly greater than that of the other, a different crystal structure might obtain.

Color

The origin of the red color of both salts warrants comment especially given that the parent compound, 4-cyano-1-methylpyridinium iodide, is yellow. Gries et al. [10] describe the hexafluorophosphate salt of the triazinium ion as colorless so the fact that crystals of **II** look red is almost certainly attributable to an electronic charge-transfer transition from iodide to the trivalent cation. Crystals of **I** are also red in transmitted light and look shiny black in reflected light. These same observations have been noted for other triiodide crystals [29-31] so this property of **I** is attributable to the anion.

SUMMARY

Two relatively unknown red compounds, 4-cyano-1-methylpyridinium triiodide and 1,1',1''-trimethyl-4,4',4''-(1,3,5-triazin-2,4,6-triyl)tripyrindinium trisiodide, were synthesized serendipitously from yellow 4-cyano-1-methylpyridinium iodide. Crystal structures and melting points were determined and described. Interaction energies for cation pairs and associated anions were calculated for the triazinium compound.

APPENDIX A. SUPPLEMENTARY DATA

CCDC 1430107,1430162,1430163 contain the supplementary crystallographic data for the salts whose structures are reported. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1

Crystallographic data.

	Compound I	Compound II
Empirical formula	C ₇ H ₇ N ₂ I ₃	C ₂₁ H ₂₁ N ₆ I ₃
CCDC number	1430107	1430162,1430163
Formula weight (g/mol)	499.85	738.14
Color, crystal shape	red, plate	red, needle
Crystal size (mm ³)	0.178 x 0.125 x 0.060	0.118 x 0.052 x 0.036
T (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	trigonal
Space group	P 2 ₁ /n	R -3
a (Å)	7.5649(6)	23.865(3)
b (Å)	15.7184(13)	23.865(3)
c (Å)	10.4723(8)	7.2660(9)
α (°)	90	90
β (°)	98.638(1)	90
γ (°)	90	120
V (Å ³)	1231.12(17)	3583.8(10)
Z	4	6
D _{calc} (Mg/m ³)	2.697	2.052
Absorption Correction	multi-scan	multi-scan
Reflections collected	35721	10708

Unique reflections	3235 ($R_{\text{int}} = 0.0407$)	1964 ($R(\text{int}) = 0.0373$)
Data / restraints / parameters	3235 / 0 / 111	1964 / 0 / 92
Final R indices	2822 data; $I > 2\sigma(I)$	1736 data; $I > 2\sigma(I)$
	$R1 = 0.0222$, $wR2 = 0.0519$	$R1 = 0.0276$, $wR2 = 0.0521$
All data	$R1 = 0.0276$, $wR2 = 0.0540$	$R1 = 0.0355$, $wR2 = 0.0557$
Weighting scheme	$w = 1 / [\sigma^2(F_o^2) + (0.0262P)^2 + 0.7229P]$ $w = 1 / [\sigma^2(F_o^2) + (0.0167P)^2 + 11.5294P]$ <p>where $P = (F_o^2 + 2F_c^2) / 3$</p>	

Table 2

Selected geometries in Compound I.

Triiodide anion bond distances and angle (pm, °)

I1-I2	293.86(3)	I2-I3	291.34(3)	I1-I2-I3	177.084(9)
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Hydrogen-bonding interactions (pm, °)

<i>D</i> ---H $\cdots$ A	<i>D</i> ---H	H $\cdots$ A	<i>D</i> $\cdots$ A	<i>D</i> ---H $\cdots$ A
C1-H1A $\cdots$ I3 ⁱ	98	310	400.9(4)	155
C1-H1C $\cdots$ I3 ⁱⁱ	98	317	410.9(4)	160
C2-H2 $\cdots$ I3 ⁱⁱⁱ	95	300	395.3(3)	178
C3-H3 $\cdots$ N2 ^{iv}	95	255	345.1(4)	159
C5-H5 $\cdots$ I2 ^v	95	315	388.2(3)	135
C6-H6 $\cdots$ I1 ^v	95	311	406.2(3)	176

r_{vdw} H 120 pm, N 155 pm, I 202 pm. Symmetry operations: i: -x, 1-y, 1-z;

ii: 0.5-x, -0.5+y, 1.5-z; iii: 1-x, 1-y, 1-z; iv: 1-x, -y, 1-z; v: -0.5+x, 0.5-y, 0.5+z.

Table 3

Selected geometries in Compound II.

Triazine ring centroid distances (pm)

Convex pair 348 Concave pair 379

Pyridine nitrogens to closest iodide (pm)

N1-I1 (convex cation, same pair) 363 N1-I1 (concave overhang) 367

Relative pyridine ring tilt and torsion about C4-C7(°)

triazine centroid-C7-C4 176.5 C7-C4-pyridine centroid 176.4

C3-C4-C7-N2 dihedral 3.1, 179.6 C5-C4-C7-N2 dihedral 2.7, -173.8

Hydrogen-bonding interactions (pm, °)

<u>D---H...A</u>	<u>D---H</u>	<u>H...A</u>	<u>D...A</u>	<u>D---H...A</u>
C1-H1B...I1 ⁱ	98	330	422.8(4)	159
C2-H2...I1 ⁱ	95	319	404.3(3)	150
C3-H3...I1 ⁱⁱ	95	317	405.6(3)	156
C5-H5...I1 ⁱⁱⁱ	95	304	386.4(3)	146
C6-H6...I1 ^{iv}	95	318	410.2(3)	163

r_{vdw} H 120 pm, N 155 pm, I 202 pm. Symmetry operations: i: 1-x, 1-y, 1-z;

ii: 0.3333+y, 0.6667-x-y, 0.6667-z; iii: 0.3333+x-y, -0.3333+x, 0.6667-z;

iv: 0.3333-x+y, 0.6667-x, 0.6667+z

Figure captions (figures attached as a Powerpoint file)

Figure 1. Unit cell of Compound I, 4-cyano-1-methylepyridinium triiodide.

Figure 2. Convex (left) and concave (right) cation pairs and octamers (cation pair plus six anions) in Compound II.

Figure 3. A column of alternating convex and concave cation pairs in Compound II with iodide anions between concave pairs.

Figure 4. View down the crystallographic *c* axis showing snowflake pattern and arrangement of iodides around cation edges.

Figure 1

Figure 2

Figure 3

Figure 4