Supporting Information: Unexpected Behaviour in Derivatives of Barluenga's Reagent, $Hal(Coll)_2X$ (Coll = 2,4,6-trimethyl pyridine, collidine; $Hal = I, Br; X = PF_6, ClO_4 \& BF_4$).

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Abstract

For the collidine analogues of Barluenga's Reagent (IPy_2BF_4) reported, a flat cation is necessary for the generation of a modulated phase, in keeping with the "Ratchet Model" theory [Kim *et al., Crystal Growth & Design*, 2014, **14**, 6294]. Attempts to study "diffuse modulation" in Br(Coll)₂ClO₄ have shown that these non-Bragg features disappear very rapidly on exposure to synchrotron radiation, an effect thought to be caused by the radiation damage disrupting the lattice vibrations that cause the modulation. This supporting information contains:

- Experimental details for single crystal X-ray diffraction data collection, structure solution and refinement.
- Explanation of the relationship between the cell settings for $I(Coll)_2 ClO_4 \& Br(Coll)_2 ClO_4$ in Polymorph I.
- Chemical schemes, displacement ellipsoid plots, selected reconstructed reciprocal lattice sections and final refinement statistics for each structure reported:
 - $I(Coll)_2 PF_6$
 - $Br(Coll)_2 PF_6$
 - $I(Coll)_2 ClO_4$ -I
 - $Br(Coll)_2ClO_4-I$
 - I(Coll)₂ClO₄-II
 - $Br(Coll)_2ClO_4-II$
 - $Br(Coll)_2 BF_4$
- Experimental details, chemical scheme, displacement ellipsoid plot, packing diagrams, selected reconstructed reciprocal lattice sections and final refinement statistics for the structure of (Coll)HBr.
- Experimental details for powder diffraction data collected on $Br(Coll)_2ClO_4$ -II, unit cell refinement with calibration data, and graphs showing the unit cell changes.

Experimental Details for

Single Crystal X-ray Diffraction Studies

Single crystal X-ray diffraction data were initially collected using a (Rigaku) Oxford Diffraction Supernova in-house diffractometer ($\lambda = 1.54184$ Å) fitted with an Oxford CryoSystems 700 Series CryoStream.¹ In general, a suitable crystal was chosen and was mounted on a 200 μ m MiTeGen loop using perfluoropolyether oil at 300 K. Typically, a hemisphere of data was collected to a resolution of 0.8 Å at 300 K prior to the sample being cooled to 100 K where the data collection was repeated. The exception to this was Br(Coll)₂PF₆, where initial data were collected under ambient conditions and a second crystal was used for the low temperature experiment.

The CrysAlisPro software was used for data collection, as well as peak hunting, indexing reflections in reciprocal space, integration of the raw frames and application of corrections including interframe scaling, Lorentz, flood field and dark current corrections. The CrysAlisPro suite was also used to examine raw images, study harvested peaks in reciprocal space and produce reconstructions of reciprocal lattice layers. All structures were initially solved *ab initio* from the integrated intensities using SuperFlip,² and refined using full-matrix least-



Figure S1: Reciprocal lattice sections hk9 reconstructed to 1.5 Å for $Br(Coll)_2ClO_4$ -II from data collected using I19-I at Diamond Light Source. The diffuse features reduce significantly in intensity over the first twenty scans; there is no visible increase in intensity in Scan 21 after an hour at 100 K in the dark.



Figure S2: Reciprocal lattice sections hk9 reconstructed to 1.5 Å for $Br(Coll)_2ClO_4$ -II from data collected using I19-I at Diamond Light Source. The diffuse features reduce significantly in intensity over the first six scans; there is no visible increase in intensity in Scan 7 after half an hour at 100 K in the dark.

squares refinement with CRYSTALS.^{3,4} For ease of comparison, for isomorphous structures, the results reported here were based on the same starting model which was modified and refined as appropriate. In some cases, the displacement ellipsoids were found to be prolate, so these structures were modelled as disordered with a split-site and competitive occupancy refinement. Hydrogen atoms were usually clearly visible in the difference Fourier map. The hydrogen atoms were positioned at geometrically sensible positions and refined using soft restraints prior to inclusion in the refinement using a riding model.⁵

Single crystal diffraction data were also collected using beamline I19-1 at Diamond Light Source.⁶ This is dual air-bearing fixed- χ diffractometer with a Dectris Pilatus 2M pixel-array photon-counting detector. Data were initially collected at 30 K using an Oxford CryoSystems HeliX,⁷ but the diffuse features seen in the laboratory were not visible. Further data were collected at 100 K to investigate the effect of radiation on crystals of Br(Coll)₂ClO₄-II. In this case, a 45° ϕ scan (equating to 45 s of exposure) was repeated twenty times. Each scan provided sufficient data to generate reconstructed reciprocal lattice sections for visual comparison, but were not designed to give sufficient information to solve the crystal structure at each step; the experiment was repeated with similar results as reported in the manuscript.

The experiment was then modified and repeated, to determine whether the loss of the

diffuse features was a temperature induced effect caused by beam heating. This time, after the twenty initial scans, one additional scan was carried out after a one hour delay with the shutter closed (Figure S1). In a variant on this, only six scans were carried out initially and the delay was only half an hour (Figure S2).

All data collected using I19-1 were initially automatically reduced using Xia2⁸ where possible, but the CrysAlisPro suite was used to examine the raw images, study harvested peaks in reciprocal space and produce reconstructions of reciprocal lattice layers. All dihedral angles between planes were calculated using PLATON,⁹ and structures were compared using MERCURY.¹⁰

For further details see the full crystallographic data (in CIF format) which are available as associated content and have been deposited with Cambridge Crystallographic Data Centre (reference codes CCDC 1853983-1853997); these data can also be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Explanation of the Cell Settings for $Hal(Coll)_2ClO_4$ -I

Despite the prima face similarity of the unit cell parameters, the structures for Polymorph I of $I(Coll)_2ClO_4$ and $Br(Coll)_2ClO_4$ reported in the literature^{11,12} are in different cell settings. It was clear from a comparison of the packing (Figure S3) that allowing for the missing disordered perchlorate in $I(Coll)_2ClO_4$, the structures of $I(Coll)_2ClO_4$ -I and $Br(Coll)_2ClO_4$ -I are essentially isomorphous.¹³ On closer examination, it became clear that data for $Br(Coll)_2ClO_4$ -I could be indexed with three related C-centred cells (Figure S4). All three cells are related through the primitive reduced cell, 11.028 Å, 14.712 Å, 19.564 Å, 82.31° , 73.63° , 67.99° , V = 2822.07 Å³. This can be transformed to give the three different C-centred cells (Table 1) using the following matrices:

$$\begin{pmatrix} h^{1} \\ k^{1} \\ l^{1} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -2 \\ 1 & 0 & 0 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$
$$\begin{pmatrix} h^{2} \\ k^{2} \\ l^{2} \end{pmatrix} = \begin{pmatrix} 1 & -2 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$
$$\begin{pmatrix} h^{3} \\ k^{3} \\ l^{3} \end{pmatrix} = \begin{pmatrix} 1 & -2 & 0 \\ 1 & 0 & 0 \\ -1 & 1 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

To ease comparison, the structures of $Br(Coll)_2ClO_4$ -I reported herein are presented in the original $I(Coll)_2ClO_4$ -I cell setting. Although the structure solved *ab initio*, coordinates from $I(Coll)_2ClO_4$ -I were used as a starting model so refinements could be more easily compared. Aside from the disorder seen in the perchlorate for $I(Coll)_2ClO_4$ -I at 300 K, $Br(Coll)_2ClO_4$ -I are isomorphous throughout the temperature range studied.



Figure S3: Comparison of the packing for the literature structures of Polymorph I of $I(Coll)_2ClO_4$ (red) and Polymorph I Br $(Coll)_2ClO_4$ (blue) viewed perpendicular to the *ac* plane.



Figure S4: Schematic of the relationship between the different unit cell settings for $Br(Coll)_2ClO_4$ -I viewed perpendicular to the *ac* plane. Lattice points in the basal plane are shown in grey.

Table 1: Unit cell parameters for the literature structure 12 of $\rm Br(Coll)_2ClO_4-I$ in the different cell settings.

	1: Original	2: BAZNAR	3: Oblique	Niggli
	AKOXON Setting	Setting	Setting	Reduced Cell
<i>a</i> /Å	27.280	27.280	37.541	11.028
$b/{ m \AA}$	11.028	11.028	11.028	14.712
$c/{ m \AA}$	22.850	23.551	22.850	19.564
$\alpha/^{\circ}$	90.00	90.00	90.00	82.31
$\beta/^{\circ}$	124.81	127.19	143.37	73.63
$\gamma/^{\circ}$	90.00	90.00	90.00	67.99
$Volume/Å^3$	5644.13	5644.13	5644.13	2822.07

$I(Coll)_2 PF_6$



Figure S5: Schematic of $I(Coll)_2 PF_6$ (top) with the displacement ellipsoid plots for the asymmetric unit at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



 $300\,\mathrm{K}:\,hk0$

 $100\,\mathrm{K}:\,hk0$





Figure S6: Reciprocal lattice sections reconstructed to $1.5\,\text{\AA}$ for $\mathrm{I(Coll)_2PF_6}.$

Compound/Identification code	$\rm I(Coll)_2 PF_6/130 lcm 18$	
Empirical formula	C16 H22 F6 I N2 P	
Formula weight	514.23	
Temperature	$300\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Triclinic; $P\overline{1}$	
Unit cell dimensions	a = 8.0754(2) Å	$\alpha = 99.537(3)^{\circ}$
	$b = 8.3550(3) \text{\AA}$	$\beta = 98.842(3)^{\circ}$
	c = 15.6634(7) Å	$\gamma = 98.269(3)^{\circ}$
Volume	$1014.16(7) \text{\AA}^3$	
Z	2	
Density (calculated)	$1.684{ m Mg/m^3}$	
Absorption coefficient	$13.680{\rm mm^{-1}}$	
F(000)	507.998	
Crystal size	$0.23 \ge 0.19 \ge 0.07 \mathrm{mm^3}$	
Theta range for data collection	5.452 to 76.049°	
Index ranges	$-7 \leqslant h \leqslant 10, -10 \leqslant k \leqslant 10$	$\leqslant 10, -19 \leqslant l \leqslant 19$
Reflections collected	9190	
Independent reflections	4174 [R(int) = 0.035]	
Completeness to theta = 72.500°	99.7%	
Absorption correction	Semi-empirical from equ	ivalents
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4173 / 0 / 235	
Goodness-of-fit on F^2	0.9047	
Final R indices $[I>2sigma(I)]$	R1 = 0.0381, wR2 = 0.1015	
R indices (all data)	R1 = 0.0404, wR2 = 0.7	1042
Largest diff. peak and hole	$1.02~{\rm and}$ -0.80 ${\rm e. \AA^{-3}}$	

Compound/Identification code	$\rm I(Coll)_2 PF_6/131lcm18$	
Empirical formula	C16 H22 F6 I N2 P	
Formula weight	514.23	
Temperature	100 K	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Triclinic; $P\overline{1}$	
Unit cell dimensions	$a = 7.9723(2) \text{\AA}$	$\alpha = 99.377(3)^{\circ}$
	b = 8.2018(3) Å	$\beta = 97.639(2)^{\circ}$
	c = 15.4695(5) Å	$\gamma = 100.448(2)^{\circ}$
Volume	967.59(5) Å ³	
Ζ	2	
Density (calculated)	$1.765\mathrm{Mg/m^3}$	
Absorption coefficient	$14.338{\rm mm}^{-1}$	
F(000)	507.998	
Crystal size	$0.23 \ge 0.19 \ge 0.07 \mathrm{mm^3}$	
Theta range for data collection	5.589 to 75.791°	
Index ranges	$-7 \leqslant h \leqslant 9, -10 \leqslant k \leqslant 10, -19 \leqslant l \leqslant 19$	
Reflections collected	8478	
Independent reflections	3933 [R(int) = 0.030]	
Completeness to theta = 72.500°	97.5%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares	s on F^2
Data / restraints / parameters	3932 / 0 / 235	
Goodness-of-fit on \mathbf{F}^2	1.0534	
Final R indices $[I>2sigma(I)]$	R1 = 0.0323, wR2 = 0.0836	
R indices (all data)	R1 = 0.0330, wR2 = 0.0)840
Largest diff. peak and hole	1.34 and $-1.18\mathrm{e}.\mathrm{\AA}^{-3}$	

$Br(Coll)_2 PF_6$



Figure S7: Schematic of $Br(Coll)_2 PF_6$ (top) with the displacement ellipsoid plots for the asymmetric unit at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



 $300\,\mathrm{K}:\,hk0$



 $100\,\mathrm{K}:\,hk0$



 $300\,\mathrm{K}:\,h0l$

 $100\,\mathrm{K}:\,h0l$



 $300\,\mathrm{K}:\,0kl$

 $100\,\mathrm{K}{:}\;0kl$

Figure S8: Reciprocal lattice sections reconstructed to $1.5\,\text{\AA}$ for $\mathrm{Br}(\mathrm{Coll})_2\mathrm{PF}_6.$

Compound/Identification code	$\rm Br(Coll)_2 PF_6/0111cm17$	
Empirical formula	C16 H22 Br F6 N2 P	
Formula weight	467.23	
Temperature	$300\mathrm{K}$	
Wavelength	1.54184\AA	
Crystal system & space group	Triclinic; $P\overline{1}$	
Unit cell dimensions	a = 8.0237(2) Å	$\alpha = 99.420(2)^{\circ}$
	b = 8.3951(2) Å	$\beta = 98.926(2)^{\circ}$
	c = 15.2556(4) Å	$\gamma = 97.070(2)^{\circ}$
Volume	$989.79(4) \text{ Å}^3$	
Z	2	
Density (calculated)	$1.568\mathrm{Mg/m^3}$	
Absorption coefficient	$4.136{\rm mm}^{-1}$	
F(000)	471.998	
Crystal size	$0.20 \ge 0.12 \ge 0.09 \mathrm{mm^3}$	
Theta range for data collection	5.404 to 75.169°	
Index ranges	$-10 \leqslant h \leqslant 10, \ -10 \leqslant k \leqslant 10, \ -19 \leqslant l \leqslant 19$	
Reflections collected	15137	
Independent reflections	3961 [R(int) = 0.023]	
Completeness to theta = 71.000°	99.2%	
Absorption correction	Semi-empirical from equ	ivalents
Refinement method	Full-matrix least-squares	s on F^2
Data / restraints / parameters	3953 / 0 / 235	
Goodness-of-fit on F^2	0.8915	
Final R indices $[I>2sigma(I)]$	R1 = 0.0383, wR2 = 0.1029	
R indices (all data)	R1 = 0.0412, wR2 = 0.1	062
Largest diff. peak and hole	0.76 and -0.36 e.Å $^{-3}$	

Compound/Identification code	$Br(Coll)_2 PF_6/074lcm18$	
Empirical formula	C16 H22 Br F6 N2 P	
Formula weight	467.23	
Temperature	$100\mathrm{K}$	
Wavelength	1.54184\AA	
Crystal system & space group	Triclinic; $P\overline{1}$	
Unit cell dimensions	$a = 7.9058(3) \text{\AA}$	$\alpha = 98.632(3)^{\circ}$
	b = 8.2573(3) Å	$\beta = 98.087(3)^{\circ}$
	c = 15.1037(6) Å	$\gamma = 100.308(3)^{\circ}$
Volume	944.74(6) Å ³	
Z	2	
Density (calculated)	$1.642{ m Mg/m^3}$	
Absorption coefficient	$4.333{\rm mm^{-1}}$	
F(000)	471.998	
Crystal size	$0.25 \ge 0.20 \ge 0.09 \text{ mm}^3$	
Theta range for data collection	5.536 to 76.527°	
Index ranges	$-9 \leqslant h \leqslant 7, -10 \leqslant k \leqslant 10, -18 \leqslant l \leqslant 19$	
Reflections collected	9313	
Independent reflections	3891 [R(int) = 0.022]	
Completeness to theta = 73.466°	99.6%	
Absorption correction	Semi-empirical from equi	valents
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3891 / 0 / 235	
Goodness-of-fit on \mathbf{F}^2	1.0387	
Final R indices $[I>2sigma(I)]$	R1 = 0.0279, wR2 = 0.0744	
R indices (all data)	R1 = 0.0283, wR2 = 0.0747	
Largest diff. peak and hole	$0.70 \text{ and } -0.42 \text{ e.} \text{\AA}^{-3}$	

$I(Coll)_2ClO_4$ -I



Figure S9: Schematic of $I(Coll)_2 ClO_4$ -I (top) with the displacement ellipsoid plots for the asymmetric unit for Polymorph I at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



Figure S10: Reciprocal lattice sections reconstructed to $1.5\,\text{\AA}$ for $\rm I(Coll)_2 ClO_4\text{-}I.$

Compound/Identification code	$\rm I(Coll)_2 ClO_4 \text{-} I/139 lcm 18\text{-} 300 K$	
Empirical formula	C16 H22 Cl I N2 O4	
Formula weight	468.72	
Temperature	$300\mathrm{K}$	
Wavelength	1.54184\AA	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 27.9017(9) Å	$\alpha=90^\circ$
	b = 11.0678(2) Å	$\beta = 126.566(5)^{\circ}$
	c = 23.4625(8) Å	$\gamma=90^\circ$
Volume	5819.3(5) Å ³	
Z	12	
Density (calculated)	$1.605\mathrm{Mg/m^3}$	
Absorption coefficient	$14.425{\rm mm}^{-1}$	
F(000)	2807.984	
Crystal size	$0.22 \ge 0.18 \ge 0.11 \mathrm{mm^3}$	
Theta range for data collection	3.940 to 76.310°	
Index ranges	$-34 \leqslant h \leqslant 34, -13 \leqslant k \leqslant 12, -13 $	$-26 \leqslant l \leqslant 29$
Reflections collected	37010	
Independent reflections	6063 [R(int) = 0.040]	
Completeness to theta = 76.310°	99.6%	
Absorption correction	Semi-empirical from equivalents	5
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6055 / 44 / 349	
Goodness-of-fit on \mathbf{F}^2	1.0316	
Final R indices $[I>2sigma(I)]$	R1 = 0.0292, wR2 = 0.0765	
R indices (all data)	R1 = 0.0330, wR2 = 0.0805	
Largest diff. peak and hole	0.79 and -0.41 e.Å $^{-3}$	

Compound/Identification code	$\rm I(Coll)_2 ClO_4 \text{-} I/139 lcm18 \text{-} 100 K$	
Empirical formula	C16 H22 Cl I N2 O4	
Formula weight	468.72	
Temperature	100 K	
Wavelength	1.54184\AA	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	$a = 27.2651(14) \text{\AA}$	$\alpha=90^{\circ}$
	b = 10.9468(3) Å	$\beta = 126.566(5)^{\circ}$
	c = 23.2069(12) Å	$\gamma=90^\circ$
Volume	$5593.9(7) \text{\AA}^3$	
Ζ	12	
Density (calculated)	$1.670\mathrm{Mg/m^3}$	
Absorption coefficient	$15.007{\rm mm}^{-1}$	
F(000)	2808	
Crystal size	$0.22 \ge 0.18 \ge 0.11 \mathrm{mm^3}$	
Theta range for data collection	4.004 to 76.107°	
Index ranges	$-33 \leqslant h \leqslant 34, -13 \leqslant k \leqslant 12, -13 $	$-26 \leqslant l \leqslant 29$
Reflections collected	34815	
Independent reflections	5833 [R(int) = 0.037]	
Completeness to theta = 76.107°	99.6%	
Absorption correction	Semi-empirical from equivalents	5
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5829 / 44 / 349	
Goodness-of-fit on F^2	0.9847	
Final R indices $[I>2sigma(I)]$	R1 = 0.0377, wR2 = 0.1057	
R indices (all data)	R1 = 0.0395, wR2 = 0.1083	
Largest diff. peak and hole	$1.63 \text{ and } -1.52 \mathrm{e. A^{-3}}$	

$Br(Coll)_2ClO_4$ -I



Figure S11: Schematic of $Br(Coll)_2ClO_4$ -I (top) with the displacement ellipsoid plots for the asymmetric unit for Polymorph I at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



Figure S12: Reciprocal lattice sections reconstructed to $1.5\,\text{\AA}$ for $\mathrm{Br}(\mathrm{Coll})_2\mathrm{ClO}_4\text{-I}.$

Compound/Identification code	$\rm Br(Coll)_2 ClO_4\text{-}I/126lcm18$	
Empirical formula	C16 H22 Br1 Cl1 N2 O4	
Formula weight	421.72	
Temperature	$300\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	$a = 27.3108(5) \text{\AA}$	$\alpha = 90^{\circ}$
	b = 11.0568(1) Å	$\beta = 127.217(3)^{\circ}$
	c = 23.5758(4) Å	$\gamma=90^\circ$
Volume	5669.4(3) Å ³	
Z	12	
Density (calculated)	$1.482\mathrm{Mg/m^3}$	
Absorption coefficient	$4.457{\rm mm^{-1}}$	
F(000)	2592	
Crystal size	$0.34 \ge 0.22 \ge 0.09 \mathrm{mm^3}$	
Theta range for data collection	3.943 to 76.118°	
Index ranges	$-33 \leqslant h \leqslant 34, -13 \leqslant k \leqslant 13, -29 \leqslant l \leqslant 29$	
Reflections collected	34084	
Independent reflections	5906 [R(int) = 0.039]	
Completeness to theta = 76.118°	99.7%	
Absorption correction	Semi-empirical from equiva	lents
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5906 / 0 / 327	
Goodness-of-fit on F^2	0.9990	
Final R indices $[I>2sigma(I)]$	R1 = 0.0341, wR2 = 0.0904	
R indices (all data)	R1 = 0.0372, wR2 = 0.0941	
Largest diff. peak and hole	$0.43 \text{ and } -0.45 \text{ e.} \text{\AA}^{-3}$	

Compound/Identification code	$\rm Br(Coll)_2 ClO_4\text{-}I/127lcm18$	
Empirical formula	C16 H22 Br1 Cl1 N2 O4	
Formula weight	421.72	
Temperature	100 K	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	$a = 26.7649(4) \text{\AA}$	$\alpha = 90^{\circ}$
	b = 10.8741(1) Å	$\beta = 126.930(2)^{\circ}$
	c = 23.3335(3) Å	$\gamma=90^\circ$
Volume	5428.59(19) Å ³	
Z	12	
Density (calculated)	$1.548\mathrm{Mg/m^3}$	
Absorption coefficient	$4.654\mathrm{mm}^{-1}$	
F(000)	2592	
Crystal size	$0.34 \ge 0.22 \ge 0.09 \mathrm{mm^3}$	
Theta range for data collection	4.001 to 76.122°	
Index ranges	$-32 \leqslant h \leqslant 33, -13 \leqslant k \leqslant 13, -29 \leqslant l \leqslant 29$	
Reflections collected	32349	
Independent reflections	5654 [R(int) = 0.028]	
Completeness to theta = 74.600°	99.8%	
Absorption correction	Semi-empirical from equiva	lents
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5654 / 0 / 327	
Goodness-of-fit on F^2	1.0181	
Final R indices $[I>2sigma(I)]$	R1 = 0.0250, wR2 = 0.0662	
R indices (all data)	R1 = 0.0255, wR2 = 0.0666	
Largest diff. peak and hole	$0.72 \text{ and } -0.42 \text{ e.} \text{\AA}^{-3}$	

$I(Coll)_2 ClO_4$ -II



Figure S13: Schematic of $I(Coll)_2 ClO_4$ -II (top) with the displacement ellipsoid plots for the asymmetric unit for Polymorph II at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



Figure S14: Reciprocal lattice sections reconstructed to 1.5 Å for $\rm I(Coll)_2 ClO_4\text{-}II.$

Compound/Identification code	$\rm I(Coll)_2 ClO_4\text{-}II/099lcm18$	
Empirical formula	C16 H22 Cl I N2 O4	
Formula weight	468.72	
Temperature	$300\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 29.1018(8) Å	$\alpha = 90^{\circ}$
	b = 8.5668(2) Å	$\beta = 100.803(3)^{\circ}$
	c = 15.9883(5) Å	$\gamma=90^\circ$
Volume	3915.39(19) Å ³	
Z	8	
Density (calculated)	$1.590\mathrm{Mg/m^3}$	
Absorption coefficient	$14.293{\rm mm}^{-1}$	
F(000)	1872.000	
Crystal size	$0.211 \ge 0.156 \ge 0.041 \mathrm{mm^3}$	
Theta range for data collection	5.391 to 76.164°	
Index ranges	$-35\leqslant h\leqslant 36,-10\leqslant k\leqslant 7,-18\leqslant l\leqslant 19$	
Reflections collected	11165	
Independent reflections	4035 [R(int) = 0.033]	
Completeness to theta = 73.879°	99.9%	
Absorption correction	Gaussian integration using indexed faces	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4027 / 88 / 257	
Goodness-of-fit on F^2	1.0051	
Final R indices $[I>2sigma(I)]$	R1 = 0.0441, wR2 = 0.1016	
R indices (all data)	R1 = 0.0441, wR2 = 0.1018	
Largest diff. peak and hole	$0.59~{\rm and}$ -0.43 ${\rm e. \AA^{-3}}$	

Compound/Identification code	$\rm I(Coll)_2 ClO_4 \text{-}II/100 lcm18$	
Empirical formula	C16 H22 Cl I N2 O4	
Formula weight	468.72	
Temperature	$100\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 29.0825(6) Å	$\alpha = 90^{\circ}$
	b = 8.5757(2) Å	$\beta = 102.602(2)^{\circ}$
	c = 15.4139(3) Å	$\gamma=90^\circ$
Volume	3751.66(14) Å ³	
Z	8	
Density (calculated)	$1.660\mathrm{Mg/m^3}$	
Absorption coefficient	$14.917{\rm mm}^{-1}$	
F(000)	1871.992	
Crystal size	$0.211 \ge 0.156 \ge 0.041 \mathrm{mm^3}$	
Theta range for data collection	5.389 to 76.341°	
Index ranges	$-36 \leqslant h \leqslant 35, -10 \leqslant k \leqslant 8, -19 \leqslant l \leqslant 16$	
Reflections collected	12365	
Independent reflections	3878 [R(int) = 0.033]	
Completeness to theta = 74.051°	99.6%	
Absorption correction	Gaussian integration using indexed faces	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3869 / 0 / 220	
Goodness-of-fit on \mathbf{F}^2	1.0089	
Final R indices $[I>2sigma(I)]$	R1 = 0.0354, wR2 = 0.0991	
R indices (all data)	R1 = 0.0396, wR2 = 0.1036	
Largest diff. peak and hole	1.21 and $-0.67\mathrm{e}.\mathrm{\AA}^{-3}$	

$Br(Coll)_2ClO_4$ -II



Figure S15: Schematic of $Br(Coll)_2ClO_4$ -II (top) with the displacement ellipsoid plots for the asymmetric unit for Polymorph II at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).





 $300\,\mathrm{K}:\,0kl$

 $100\,\mathrm{K}{:}\;0kl$

Figure S16: Reciprocal lattice sections reconstructed to $1.5\,\text{\AA}$ for $\mathrm{Br(Coll)_2ClO_4}\text{-II}.$

Compound/Identification code	$\rm Br(Coll)_2 ClO_4\text{-}II/067yk14\text{-}300K$	
Empirical formula	C16 H22 Br Cl N2 O4	
Formula weight	421.72	
Temperature	$300\mathrm{K}$	
Wavelength	1.54184 Å	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 28.8059(14) Å	$\alpha = 90^{\circ}$
	b = 8.5296(3) Å	$\beta = 99.565(4)^{\circ}$
	$c = 15.8383(7) \text{\AA}$	$\gamma = 90^{\circ}$
Volume	3837.4(3) Å ³	
Z	8	
Density (calculated)	$1.460\mathrm{Mg/m^3}$	
Absorption coefficient	$4.389{ m mm^{-1}}$	
F(000)	1728	
Crystal size	$0.35 \ge 0.15 \ge 0.08 \mathrm{mm^3}$	
Theta range for data collection	3.111 to 76.785°	
Index ranges	$-31 \leqslant h \leqslant 36, \ -10 \leqslant k \leqslant 10, \ -10$	$19 \leqslant l \leqslant 16$
Reflections collected	20990	
Independent reflections	3997 [R(int) = 0.047]	
Completeness to theta = 75.249°	99.5%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on ${\rm F}^2$	
Data / restraints / parameters	3981 / 88 / 257	
Goodness-of-fit on F^2	0.9997	
Final R indices $[I>2sigma(I)]$	R1 = 0.0456, wR2 = 0.1257	
R indices (all data)	R1 = 0.0517, wR2 = 0.1369	
Largest diff. peak and hole	$0.44 \text{ and } -0.54 \text{ e.} \text{\AA}^{-3}$	

Compound/Identification code	$\rm Br(Coll)_2 ClO_4-II/067yk14-100K$	
Empirical formula	C16 H22 Br Cl N2 O4	
Formula weight	421.72	
Temperature	100 K	
Wavelength	1.54184\AA	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 28.8168(10) Å	$\alpha = 90^{\circ}$
	b = 8.5588(2) Å	$\beta = 102.549(3)^{\circ}$
	c = 15.2931(5) Å	$\gamma=90^\circ$
Volume	3681.7(2) Å ³	
Z	8	
Density (calculated)	$1.522\mathrm{Mg/m^3}$	
Absorption coefficient	$4.575\mathrm{mm}^{-1}$	
F(000)	1728	
Crystal size	$0.35 \ge 0.15 \ge 0.08 \mathrm{mm^3}$	
Theta range for data collection	3.142 to 76.248°	
Index ranges	$-30 \leqslant h \leqslant 36, -10 \leqslant k \leqslant 10, -19 \leqslant l \leqslant 16$	
Reflections collected	19843	
Independent reflections	3823 [R(int) = 0.037]	
Completeness to theta = 74.723°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3807 / 0 / 304	
Goodness-of-fit on F^2	0.9978	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1443	
R indices (all data)	R1 = 0.0567, wR2 = 0.1504	
Largest diff. peak and hole	$0.75~\mathrm{and}$ -1.16 e.Å $^{-3}$	

$Br(Coll)_2BF_4$



Figure S17: Schematic of $Br(Coll)_2BF_4$ (top) with the displacement ellipsoid plots for the asymmetric unit at 300 K and 100 K drawn at 50% probability (middle and bottom respectively).



 $300\,\mathrm{K}:\,hk0$





 $300\,\mathrm{K}:\,h0l$

 $100\,\mathrm{K}:\,h0l$



 $300\,\mathrm{K}:\,0kl$

 $100\,\mathrm{K}{:}\;0kl$

Figure S18: Reciprocal lattice sections reconstructed to 1.5 Å for Br(Coll)₂BF₄.

Compound/Identification code	$\mathrm{Br}(\mathrm{Coll})_{2}\mathrm{BF}_{4}/099\mathrm{kec}14\text{-}300\mathrm{K}$	
Empirical formula	C16 H22 B Br F4 N2	
Formula weight	409.07	
Temperature	$300\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 29.0149(3) Å	$\alpha = 90^{\circ}$
	b = 8.50144(7) Å	$\beta = 100.7977(10)^{\circ}$
	c = 15.54176(17) Å	$\gamma=90^\circ$
Volume	$3765.79(7) \mathrm{\AA^3}$	
Z	8	
Density (calculated)	$1.443\mathrm{Mg/m^3}$	
Absorption coefficient	$3.321\mathrm{mm}^{-1}$	
F(000)	1664	
Crystal size	$0.34 \ge 0.31 \ge 0.29 \mathrm{mm^3}$	
Theta range for data collection	3.101 to 76.390°	
Index ranges	$-36 \leqslant h \leqslant 36, -10 \leqslant k \leqslant 10,$	$-18\leqslant l\leqslant 19$
Reflections collected	41023	
Independent reflections	3935 [R(int) = 0.039]	
Completeness to theta = 74.863°	99.8%	
Absorption correction	Semi-empirical from equivalent	ts
Refinement method	Full-matrix least-squares on F	2
Data / restraints / parameters	3920 / 88 / 258	
Goodness-of-fit on F^2	1.0071	
Final R indices $[I>2sigma(I)]$	R1 = 0.0345, wR2 = 0.0997	
R indices (all data)	R1 = 0.0367, wR2 = 0.1023	
Largest diff. peak and hole	$0.33~{\rm and}~\text{-}0.32{\rm e.\AA^{-3}}$	

Compound/Identification code	$\mathrm{Br}(\mathrm{Coll})_2\mathrm{BF}_4/099\mathrm{kec}14\text{-}100\mathrm{K}$	
Empirical formula	C16 H22 B Br F4 N2	
Formula weight	409.07	
Temperature	$100\mathrm{K}$	
Wavelength	$1.54184\mathrm{\AA}$	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	a = 28.9753(5) Å	$\alpha = 90^{\circ}$
	b = 8.47823(11) Å	$\beta = 102.8782(19)^{\circ}$
	c = 15.0337(3) Å	$\gamma = 90^{\circ}$
Volume	3600.28(11) Å ³	
Z	8	
Density (calculated)	$1.509\mathrm{Mg/m^3}$	
Absorption coefficient	$3.474{\rm mm}^{-1}$	
F(000)	1664	
Crystal size	$0.34 \ge 0.31 \ge 0.29 \mathrm{mm^3}$	
Theta range for data collection	3.129 to 76.156°	
Index ranges	$-36 \leqslant h \leqslant 36, \ -10 \leqslant k \leqslant 10,$	$-18\leqslant l\leqslant 18$
Reflections collected	29348	
Independent reflections	3728 [R(int) = 0.035]	
Completeness to theta = 73.110°	99.6%	
Absorption correction	Semi-empirical from equivalen	ts
Refinement method	Full-matrix least-squares on F	2
Data / restraints / parameters	3713 / 0 / 304	
Goodness-of-fit on \mathbf{F}^2	1.0044	
Final R indices $[I>2sigma(I)]$	R1 = 0.0431, wR2 = 0.1078	
R indices (all data)	R1 = 0.0442, wR2 = 0.1089	
Largest diff. peak and hole	$0.98~{\rm and}$ -0.80 e. Å $^{-3}$	

(Coll)HBr

The Cambridge Structural Database¹⁴ indicated that (Coll)HBr had not been previously reported, thus an attempt was made to synthesise it. A sample was prepared by adding a small quantity of HBr to liquid collidine which yielded a white precipitate. Crystals were grown by recrystallisation from dichloromethane.



Figure S19: Schematic of (Coll)HBr (left) with the displacement ellipsoid plot at 150 K drawn at 50% probability (right). Symmetry equivalents are shown for clarity and are marked with a prime.

Single crystal X-ray diffraction data were collected using a (Rigaku) Oxford Diffraction Supernova in-house diffractometer ($\lambda = 1.54184$ Å) at 150 K¹ as described above. These data indexed with a hexagonal cell of a = 8.623 Å, c = 6.898 Å, volume = 443.9 Å. A hemisphere of data was collected to a resolution of 0.8 Å and processed using CrysAlisPro based on the hexagonal cell. The structure solved to give layers of collidinium bromide on a pseudohexagonal lattice (Figure S20). These stacked in an ABAB arrangement with channels containing bromide ions separated by $\pi - \pi$ stacked collidinium ions. Although it was possible to get a solution, it gave a highly disordered structure imposed by the hexagonal, P6₃/mmc, space group symmetry. Examination of the reconstructed reciprocal lattice sections indicated a small amount of diffuse scattering, particularly in the 0kl and h0l layers was identified (Figure S21); it was thought this might indicate the presence of a frustrated system.

Further inspection of the data suggested the possibility of an alternative, lower symmetry (Figure S22) with twinning by pseudo-merohedry, and the structure was solved in the monoclinic space group, C2/c, with a unit cell of a = 8.6217(6) Å, b = 14.9357(9) Å,



Figure S20: (Coll)HBr showing a single sheet and the pseudo-hexagonal packing broken only by the nitrogen atom (top left); the ABAB stacking of the sheets (bottom left; sheets are colour-coded to draw the eye), and the channels formed by the $\pi - \pi$ stacked collidinium ions (right).



Figure S21: Reciprocal lattice sections reconstructed to 1.5 Å for (Coll)HBr.



Figure S22: Projection down the c^* direction showing the relationship between the hexagonal cell (a = 8.623 Å, c = 6.898 Å; shown in blue) and the monoclinic cell (a = 8.622 Å, b = 14.936 Å, c = 6.89 Å, $\beta = 90^{\circ}$; shown in red) for (Coll)HBr.

c = 6.8943(4) Å, $\beta = 89.993(5)^{\circ}$, volume = 887.79(10) Å. This solution exhibited prolate ellipsoids and the relative size suggests there may still be a small degree of disorder present, which could account for the weak diffuse scattering discussed above. It was thought that the two-fold rotation axis that relates the two halves of the collidinium cation could be responsible for the prolate ellipsoids and the true symmetry could be actually be even lower, Cc or even $P\overline{1}$, but the quality of the data due to the twinning meant it was not possible to confirm this and in lower symmetry space groups the refinement became unstable. The two twin components were related by a rotation of 180° rotation about [1 1 0] direct lattice direction according to the twin law:

$$\begin{pmatrix} -0.500 & 0.500 & 0.000 \\ 1.500 & 0.500 & 0.000 \\ 0.000 & 0.000 & -1.000 \end{pmatrix}$$

Compound/Identification code	(Coll)HBr/119lcm18	
Empirical formula	C8 H12 Br ${\rm N}$	
Formula weight	202.09	
Temperature	$150\mathrm{K}$	
Wavelength	0.71073\AA	
Crystal system & space group	Monoclinic; $C2/c$	
Unit cell dimensions	$a = 8.6217(6) \text{\AA}$	$\alpha = 90^{\circ}$
	b = 14.9357(9) Å	$\beta = 90.007(5)^\circ$
	$c = 6.8943(4) \text{\AA}$	$\gamma=90^\circ$
Volume	887.79(10) Å ³	
Z	4	
Density (calculated)	$1.512{ m Mg/m^3}$	
Absorption coefficient	$4.559\mathrm{mm}^{-1}$	
F(000)	408	
Crystal size	$0.28 \ge 0.20 \ge 0.09 \mathrm{mm^3}$	
Theta range for data collection	2.728 to 29.826°	
Index ranges	$-11 \leqslant h \leqslant 11, -19 \leqslant k$	$\leqslant 20, -9 \leqslant l \leqslant 9$
Reflections collected	8478	
Independent reflections	3933 [R(int) = 0.030]	
Completeness to theta = 26.545°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	938 / 88 / 53	
Goodness-of-fit on F^2	0.9991	
Final R indices $[I>2sigma(I)]$	R1 = 0.0592, wR2 = 0.1048	
R indices (all data)	R1 = 0.0592, wR2 = 0.1048	
Largest diff. peak and hole	$0.75 \text{ and } -0.81 \text{ e.} \text{Å}^{-3}$	

Experimental Details for

Synchrotron Powder Diffraction Studies

A sample of $BrColl_2ClO_4$ was mounted on a 0.3 mm diameter capillary by coating the capillarv with Atrixo[®] brand hand cream and rolling the capillary in a small quantity of the sample. The sample was only lightly ground because substantial grinding leads to breakdown of the sample. This method¹⁵ for mounting samples on capillaries when the crystals are hard to pack inside is well established at the I11 beamline and generally leads to good results. The capillary was mounted on the spinner and exposed to the X-ray beam. The capillary was placed in the path of the cryostream set to 300 K), which was used in an attempt to minimise any beam-heating effects. Powder diffraction data was collected using the Mythen[®] Position Sensitive Detector (PSD) on the I11 beamline at Diamond Light Source.^{16,17} Two 5 s scans were summed together in order to compensate for gaps in the data that would otherwise appear at the position of the junctions in the detector. This resulted in effective scan time of approximately 10.9 s. The sample was measured continuously for 500 scans (approximately 90 min). Data were collected at the zirconium edge giving a refined wavelength of 0.686907 Å (18.0 keV). This was chosen in order to mimic the conditions of the single crystal measurement performed on I19 as closely as possible. The sample was exposed to approximately $157000 \text{ photons.s}^{-1}$.

The sample is strongly absorbing because the X-ray beam wavelength is close to the absorption edge of bromine (Figure S23). Peak splitting was observed in the powder diffraction pattern (Figure S24). Due to the highly granular nature of the sample, the data were re-binned using the comparatively large bin size of 0.02° in order to ease Pawley/Rietveld analysis of this data. Data for graphical display was background subtracted using a program written by Dr A. Jupe, which implements the Brückner background subtraction method.¹⁹ The contour maps show that illuminating the sample with X-rays generally caused the peaks to shift to lower angle (indicating expansion of the lattice parameters) up to $t \sim 20$ min, at



Figure S23: Absorption plot for $\text{BrColl}_2\text{ClO}_4$ as a function of wavelength, calculated using online utility based on the Absorb/FPrime software.¹⁸ The sample density and radius were approximated (being hard to calculate due to the sample mounting method), so the ordinate should be considered to be in arbitrary units.

which point, the crystal decomposes to phases with a different crystal structure.

A powder X-ray diffraction pattern measured at $t \sim 2774$ s (~ 46 min) was analysed in order to identify the products of sample decomposition. It was found that the primary crystalline phase present was 2,4,6-trimethylpyridinium perchlorate (CSD REFCODE KUWHOA).²⁰ This phase proved to give a reasonable intensity match as well as fitting peak positions (atom positions and thermal displacement parameters were not refined). Comparison of the components present in the sample before and after X-ray induced decomposition suggested that a phase containing bromine and collidinium should also be present. It was hypothesised that this could be CollHBr. A search of the Cambridge Structural Database¹⁴ indicated that this phase has not been previously reported. Therefore, an attempt was made to synthesise this compound and the structure was determined from a crystal resulting from this synthesis (*vide supra*). This structure did not match the peaks in the powder diffraction pattern that could not be accounted for by BrColl₂ClO₄ or CollHClO₄ (indicated by an asterisk in Figure S25). This does not preclude the possibility that CollHBr is a constituent of the decomposed sample, however; it is very possible that the structure of CollHBr would



Figure S24: The powder X-ray diffraction pattern of $BrColl_2ClO_4$ at t 0 measured using the Mythen PSD on the I11 beamline. The inset emphasises the split nature of the peaks.

be different when generated by decomposition to that when grown by crystallisation from solution.



Figure S25: Rietveld fit²¹ for CollHClO₄, to data measured at $t \sim 2774$ s (~ 46 min). The asterisks indicate the position of peaks possibly attributable to CollHBr.

Lattice parameters of $\text{BrColl}_2\text{ClO}_4$ (Figure S26) were extracted using a sequential Pawley refinement²² implemented in TOPAS Academic, version 5.3.²³ This allowed the changes in the first ~ 1800 s (30 min) to be parameterised, after this the diffraction pattern was dominated by the decomposition products (as shown in the contour maps). The refined



Figure S26: Lattice parameters for $\text{BrColl}_2\text{ClO}_4$ extracted using a sequential Pawley refinement. The refined parameters are only reliably determined up to ~ 12 min, as indicated by the plot of χ^2 and the error bars.

parameters are only reliably determined up to ~ 12 min (as indicated by the plot of χ^2 vs time). Starting model: a = 28.81 Å, b = 8.53 Å, c = 15.83 Å; $\beta = 99.57^{\circ}$; space group = C2/c.

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