Supplemental Information

A Layered Heterometallic Iodoplumbate Containing a Novel Pb₃Cu₆I₁₆ Net: Structure and Optical Properties

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Structure Determination:

X-ray diffraction intensity data from a red blocklike crystal were measured at 150(1) K on a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å).¹ Raw area detector data frame integration was performed with SAINT+.¹ Final unit cell parameters were determined by least-squares refinement of 6561 strong reflections from the data set. Analysis of the data showed negligible crystal decay during collection. An absorption correction based on the multiple measurement of equivalent reflections was applied to the data with SADABS.¹ Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXTL.²

The compound crystallizes in the trigonal/hexagonal crystal system. The hexagonal Laue class 6/m was clearly indicated by Rint statistics. Systematic absences in the intensity data indicated the presence of a 6_3 screw axis. The space group P6₃/m was eventually confirmed by the successful solution and refinement of the structure. The asymmetric unit consists of $\frac{1}{3}$ of one $Co(phen)_3^{2+}$ cation located on a C₃ axis of rotation (Co1 on the Wyckoff 4f site), half of a Pb atom on a mirror plane (6h site), a Cu atom on a general position, five independent iodine atom positions and $\frac{1}{3}$ of an ethanol molecule disordered about a position of 6 (S₃) symmetry. Iodine atoms I1 and I5 are located on C₃ axes, I3 and I4 are located on mirror planes and I2 is located on a general position. The I3 position requires further comment. Refinement of I3 as a single atomic position resulted in an inflated displacement parameter several times larger than reasonable. A large buildup of electron density peak was also observed within 1 Å of I3. After some trials, this site was better refined as a split iodine position I3A/I3B. Unconstrained isotropic refinement of the two split sites resulted in occupancies of 0.57(1)/0.43(1), supporting the split model. Eventually this site was refined anisotropically with the total occupancy of the 13 site constrained to sum to unity. Three distance restraints were used to model the disordered ethanol molecule, and these atoms were refined with a common isotropic displacement All other non-hydrogen atoms were refined with anisotropic displacement parameter. parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.

 (1) SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
(2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Identification code	mcb021as		
Empirical formula	C74 H54 Co2 Cu6 I16 N12 O	Pb3	
Formula weight	4278.36		
Temperature	150(1) K		
Wavelength	0.71073 Å		
Crystal system	Hexagonal		
Space group	P6 ₃ /m		
Unit cell dimensions	a = 14.7797(3) Å	α= 90°.	
	b = 14.7797(3) Å	β= 90°.	
	c = 25.3168(9) Å	$\gamma = 120^{\circ}$.	
Volume	4789.3(2) Å ³		
Z	2		
Density (calculated)	2.967 Mg/m ³		
Absorption coefficient	12.095 mm ⁻¹		
F(000)	3824		
Crystal size	0.22 x 0.18 x 0.15 mm ³		
Theta range for data collection	1.59 to 28.30°.		
Index ranges	-19<=h<=19, -19<=k<=19, -3	1<=1<=33	
Reflections collected	44405		
Independent reflections	4068 [R(int) = 0.0489]		
Completeness to theta = 28.30°	100.0 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	1.0000 and 0.5738		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4068 / 3 / 186		
Goodness-of-fit on F ²	1.109		
Final R indices [I>2sigma(I)]	R1 = 0.0246, WR2 = 0.0555		
R indices (all data)	R1 = 0.0289, wR2 = 0.0569		
Largest diff. peak and hole	1.180 and -0.777 e.Å ⁻³		

Table S1. Crystal data and structure refinement for mcb021as.

	x	У	Z	U(eq)
 Pb(1)	2538(1)	4699(1)	7500	30(1)
I(1)	3333	6667	6677(1)	24(1)
I(2)	1868(1)	3153(1)	6530(1)	26(1)
I(3A)	4929(7)	5410(8)	7500	49(1)
I(3B)	4861(9)	5170(30)	7500	60(2)
I(4)	-743(1)	1158(1)	7500	19(1)
I(5)	0	0	6029(1)	22(1)
Cu(1)	775(1)	1252(1)	6870(1)	26(1)
Co(1)	6667	3333	5357(1)	15(1)
C(1)	5437(3)	3726(3)	4453(2)	20(1)
C(2)	5250(3)	4374(3)	4118(2)	25(1)
C(3)	5689(3)	5414(3)	4239(2)	26(1)
C(4)	6294(3)	5808(3)	4702(2)	22(1)
C(5)	6778(3)	6878(3)	4866(2)	27(1)
C(6)	7320(3)	7209(3)	5322(2)	30(1)
C(7)	7439(3)	6497(3)	5659(2)	23(1)
C(8)	7979(3)	6787(3)	6139(2)	32(1)
C(9)	8096(4)	6064(4)	6427(2)	32(1)
C(10)	7679(3)	5049(3)	6230(2)	25(1)
C(11)	7027(3)	5452(3)	5498(2)	19(1)
C(12)	6427(3)	5099(3)	5017(2)	19(1)
N(1)	6017(2)	4073(2)	4886(1)	18(1)
N(2)	7159(2)	4743(2)	5777(1)	19(1)
C(1S)	5990(30)	4130(30)	7500	96(6)
C(2S)	6770(20)	3830(20)	7500	96(6)
O(1S)	7840(20)	4260(20)	7500	96(6)

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å²x 10^3) for mcb021as. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.





[001] (top) and [100] (bottom) views of adjacent $Co(phen)_3^{2+}$ and $Pb_3Cu_6I_{16}^{4-}$ layers.



Figure S2 50% probability ellipsoid plot of the $Cu_6I_{11}^{5-}$ subunit.



Figure S3. 50% probability ellipsoid plot of the $Pb_3I_{11}^{5-}$ subunit. Local point symmetry is -6 (S₃).



Figure S4. Observed powder X-ray diffraction pattern (bottom) and simulated powder X-ray diffraction pattern (top).