## Supplemental Information

# A Layered Heterometallic Iodoplumbate Containing a Novel $\mathbf{P b}_{3} \mathbf{C u}_{6} \mathbf{I}_{16}$ 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 $\alpha$ radiation, $\lambda=0.71073 \AA$ ). ${ }^{1}$ 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 $\mathrm{F}^{2}$ were performed with SHELXTL. ${ }^{2}$

The compound crystallizes in the trigonal/hexagonal crystal system. The hexagonal Laue class $6 / \mathrm{m}$ was clearly indicated by $\mathrm{R}_{\text {int }}$ statistics. Systematic absences in the intensity data indicated the presence of a $6_{3}$ screw axis. The space group $\mathrm{P}_{3} / \mathrm{m}$ was eventually confirmed by the successful solution and refinement of the structure. The asymmetric unit consists of $1 / 3$ of one $\mathrm{Co}(\mathrm{phen}){ }_{3}{ }^{2+}$ cation located on a $\mathrm{C}_{3}$ axis of rotation (Co1 on the Wyckoff 4 f site), half of a Pb atom on a mirror plane ( 6 h site), a Cu atom on a general position, five independent iodine atom positions and $1 / 3$ of an ethanol molecule disordered about a position of $\overline{6}\left(\mathrm{~S}_{3}\right)$ symmetry. Iodine atoms I1 and I5 are located on $\mathrm{C}_{3}$ 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 $1 \AA$ 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 I3 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 parameter. All other non-hydrogen atoms were refined with anisotropic displacement 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.

Table S1. Crystal data and structure refinement for mcb021as.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=28.30^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [I>2sigma(I)]
R indices (all data)
Largest diff. peak and hole
mcb021as
C74 H54 Co2 Cu6 I16 N12 O Pb3
4278.36

150(1) K
$0.71073 \AA$
Hexagonal
$\mathrm{P}_{3} / \mathrm{m}$
$\mathrm{a}=14.7797(3) \AA \quad \alpha=90^{\circ}$.
$\mathrm{b}=14.7797(3) \AA \quad \beta=90^{\circ}$.
$\mathrm{c}=25.3168(9) \AA \quad \gamma=120^{\circ}$.
4789.3(2) $\AA^{3}$

2
$2.967 \mathrm{Mg} / \mathrm{m}^{3}$
$12.095 \mathrm{~mm}^{-1}$
3824
$0.22 \times 0.18 \times 0.15 \mathrm{~mm}^{3}$
1.59 to $28.30^{\circ}$.
$-19<=\mathrm{h}<=19,-19<=\mathrm{k}<=19,-31<=\mathrm{l}<=33$
44405
$4068[\mathrm{R}(\mathrm{int})=0.0489]$
100.0 \%

Semi-empirical from equivalents
1.0000 and 0.5738

Full-matrix least-squares on $\mathrm{F}^{2}$
4068 / 3 / 186
1.109
$\mathrm{R} 1=0.0246, \mathrm{wR} 2=0.0555$
$R 1=0.0289, w R 2=0.0569$
1.180 and -0.777 e. $\AA^{-3}$

Table S2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for mcb021as. $U(e q)$ is defined as one third of the trace of the orthogonalized $U^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{Pb}(1)$ | 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) |
| $\mathrm{Cu}(1)$ | 775(1) | 1252(1) | 6870(1) | 26(1) |
| $\mathrm{Co}(1)$ | 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) |
| $\mathrm{O}(1 \mathrm{~S})$ | 7840(20) | 4260(20) | 7500 | 96(6) |



Figure S1.
[001] (top) and [100] (bottom) views of adjacent $\mathrm{Co}(\text { phen })_{3}{ }^{2+}$ and $\mathrm{Pb}_{3} \mathrm{Cu}_{6} \mathrm{I}_{16}{ }^{4-}$ layers.


Figure S2
$50 \%$ probability ellipsoid plot of the $\mathrm{Cu}_{6} \mathrm{I}_{11}{ }^{5-}$ subunit.


Figure S3. $50 \%$ probability ellipsoid plot of the $\mathrm{Pb}_{3} \mathrm{I}_{11}{ }^{5-}$ subunit. Local point symmetry is -6 $\left(\mathrm{S}_{3}\right)$.


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

