Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Supporting Information

Chloride carbodiimide $K_{12}Pb_{51}(CN_2)_{30}Cl_{54}$ with an unprecedented 45 Å unit cell axis and a large birefringence

Xianghe Meng,[a,c] Fei Liang,[a,c] Wenlong Yin,*[b] Zheshuai Lin[a], and Mingjun Xia,*[a]

[a] Beijing Center for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[b] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

[c] University of Chinese Academy of sciences, Beijing 100049, China

Experimental Section

Single crystal structure determination. The single-crystal X-ray diffraction data was gathered on a Rigaku AFC10 single-crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ= 0.71073 Å) and Saturn CCD detector at 120 K for **1**. The intensity data, data reduction and cell refinement were captured by the CrystalClear program. The crystal structure was settled by the direct method with grogram SHELXS-2017 and further refined by full matrix least squares on F^2 by SHELXL-2017 programs.[1] The structure was confirmed by using the ADDSYM algorithm from the program PLATON with no higher symmetry was discovered.[2] The crystallographic data and refinement are summarized in Table S1. The fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table S2. The atomic displacement parameters are listed in Table S3. The bond lengths and angles are presented in Table S4.

Elemental analysis. The target crystal was carefully selected on the sample platform and measured using a field-emission scanning electron microscope (Hitachi S-4800) equipped with an energy-dispersive spectrometry detector.

Scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis. The morphology of the crystals is analyzed by field emission scanning electron microscopy (SEM, Hitachi S-4800) at an accelerating voltage of 10 kV, and the energy-dispersive X-ray spectroscopy (EDS) was used to analyze the elemental distribution.

Thermal analysis. The different scanning calorimetry (DSC) analysis was performed on NETZSCH STA 409 CD thermal analyzer under N_2 flow with a sample heating rate of 20 °C/min from room temperature to 700 °C.

Powder X-ray diffraction. The powder X-ray diffraction (PXRD) data of **1** was collected on Bruker D8 Focus diffractometer equipped with Cu Kα radiation(λ=1.5418 Å) in the 2θ range of 7-70° at room temperature.

UV–vis–NIR diffuse reflectance spectrum. The UV–vis–NIR diffuse reflectance spectra was measured in the range 200 nm to 1200 nm by a Perkin-Elmer Lambda 900 UV–vis-NIR spectrometer.

Infrared spectrum. Infrared (IR) spectroscopy was collected on a Varian Excalibur 3100 spectrometer at the range from 400 cm^{-1} to 4000 cm^{-1}. **1** and KBr samples with mass ratio about 1:100 were mixed thoroughly and rolled into transparent sheets for testing.

First principles computational method. The first-principles calculations were performed at the atomic level in the framework of density functional theory (DFT) for **1** crystal implemented in CASTEP program[3], which has been applied on metal cyanurates successfully in previous work[4]. The total energy and energy band calculations with fixed cell constants using generalized gradient approximation (GGA-PBE)[5] and hybrid HSE06 exchange-correlation potentials[6] were performed, and the ion-electron interactions were modeled by the ultra-soft pseudopotentials[7] for all elements, including K $3s^2 3p^6 4s^1$, Cd $4d^{10}5s^2$, C $2s^2 2p^2$, N $2s^2 2p^3$ and O $2s^2 2p^4$ valence electrons, respectively. In order to ensure the sufficient accuracy of the calculated results, the kinetic energy cutoff of 500 eV

and Monkhorst-Pack k-point meshes[8] spanning less than 0.04$Å^{-3}$ in the Brillouin zone were chosen. In addition, a scissors operator was adopted as the difference between the HSE06 and PBE bandgaps to obtain linear optical properties.

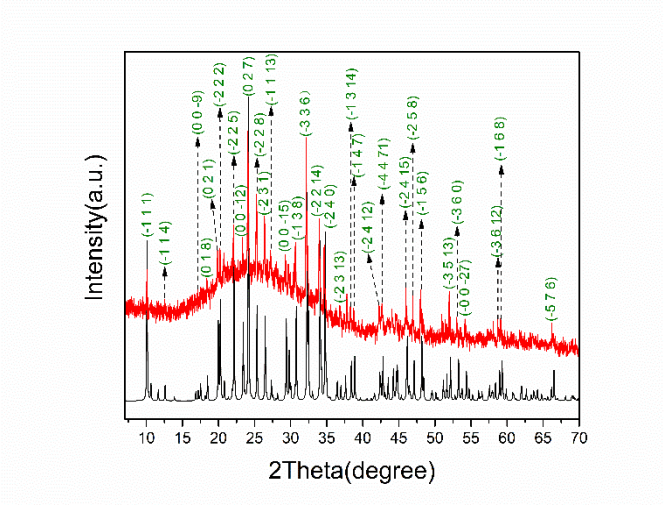

Figure S1. Experimental and calculated XRD patterns of **1.**

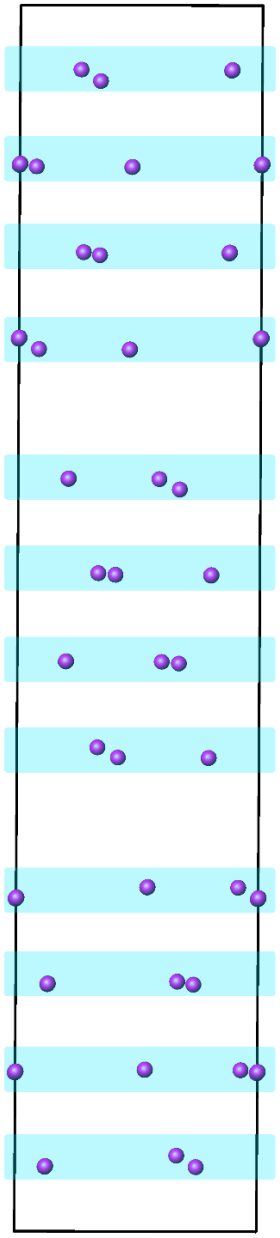

Figure S2. The stack arrangements of the twelve Pb layers along *c* axis in **1**.

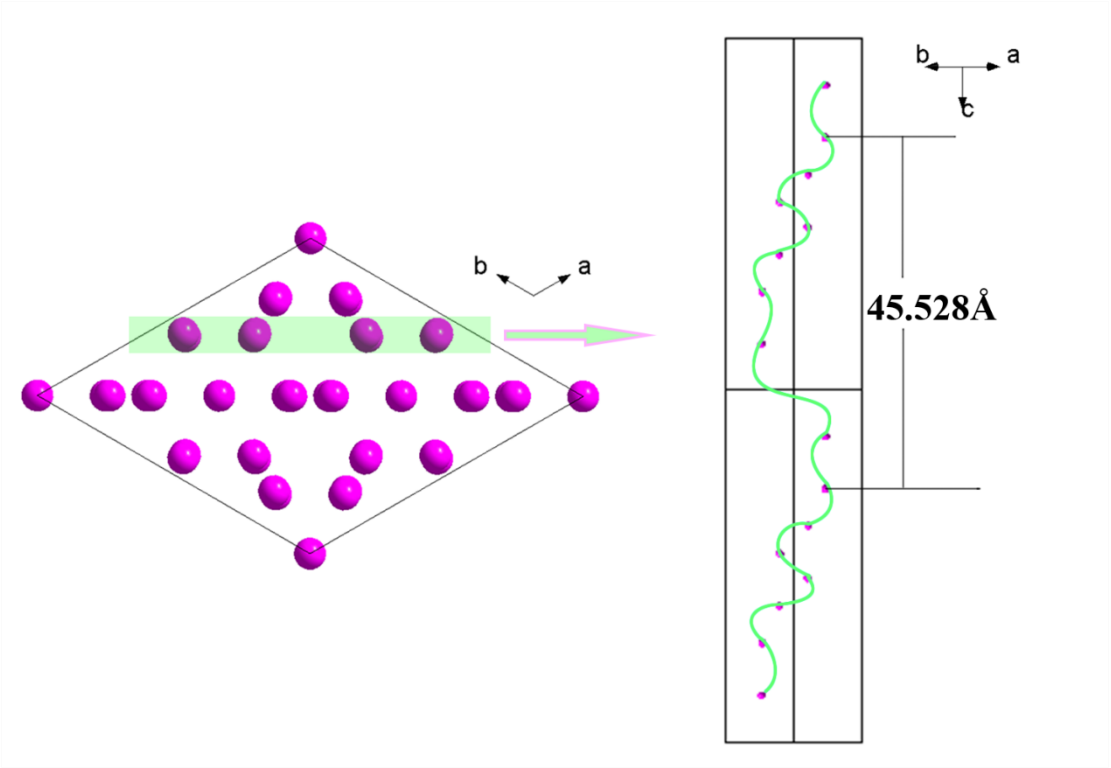

Figure S3. The rotation of Pb^{2+} cations along *c* axis.

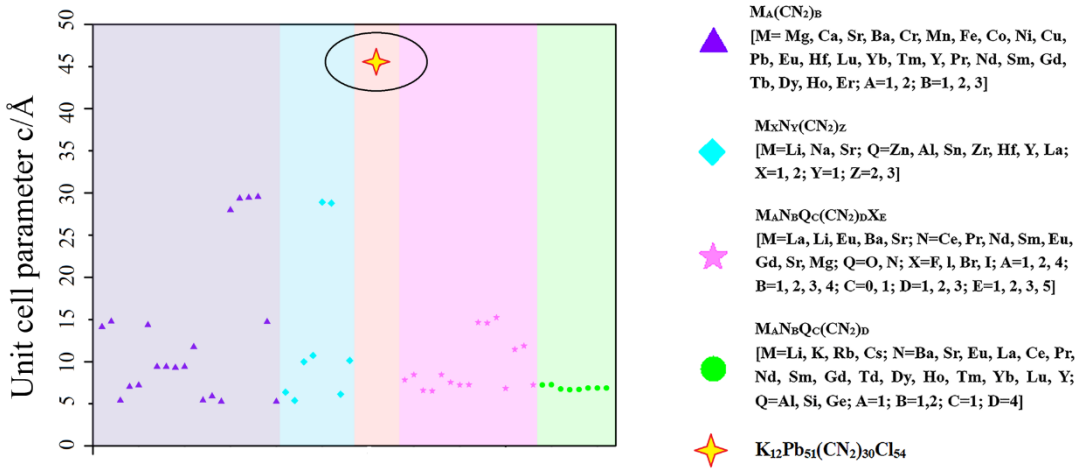

Figure S4. The unit cell parameters of the reported carbodiimides.

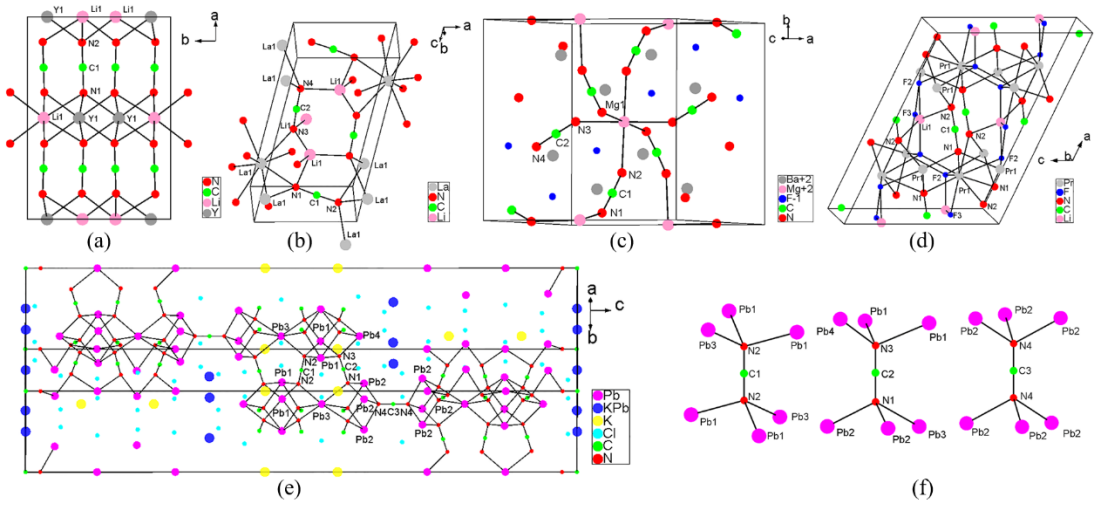

Figure S5. Crystal structures of (a) $LiY(CN_2)_2$, (b) $LiLa(CN_2)_2$, (c) $Ba_4Mg(CN_2)_4F_2$, (d) $LiPr_2(CN_2)_2F_3$ and (e) **1**. (f) The coordination environment of CN_2 in **1**.

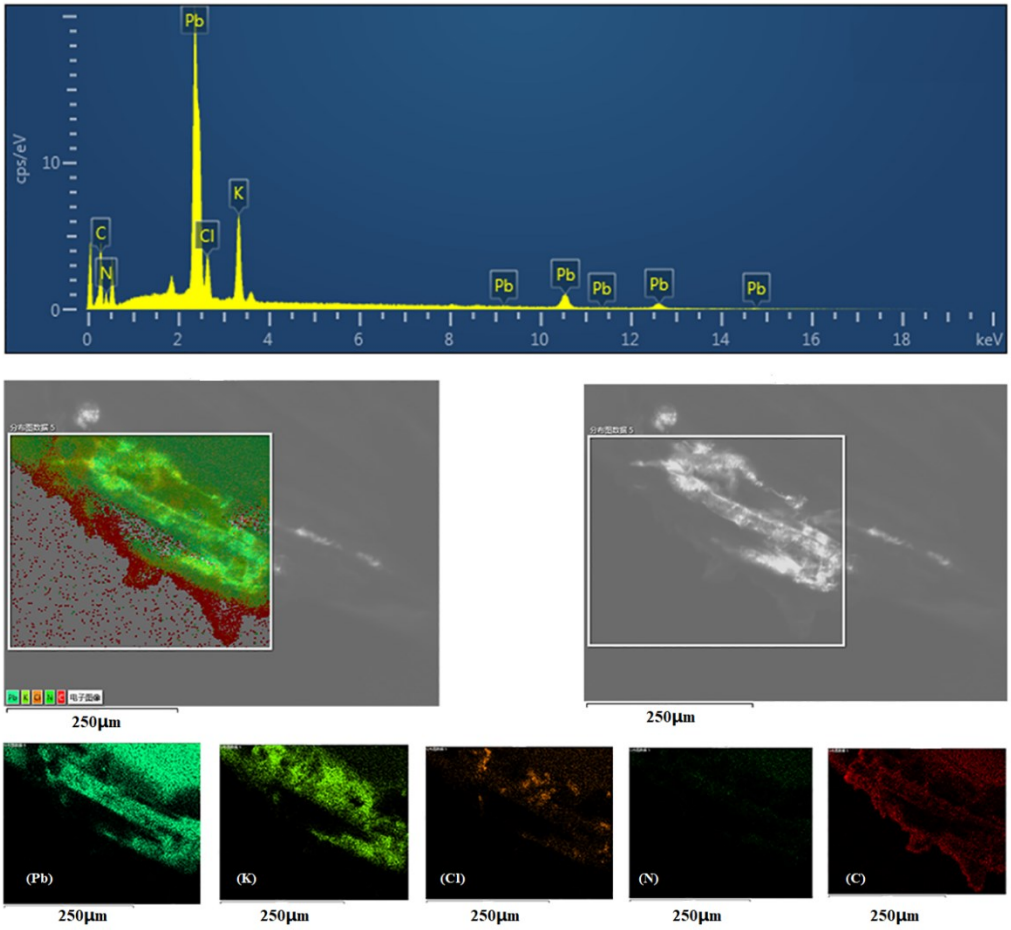

Figure S6. Elemental analysis spectrum of **1**.

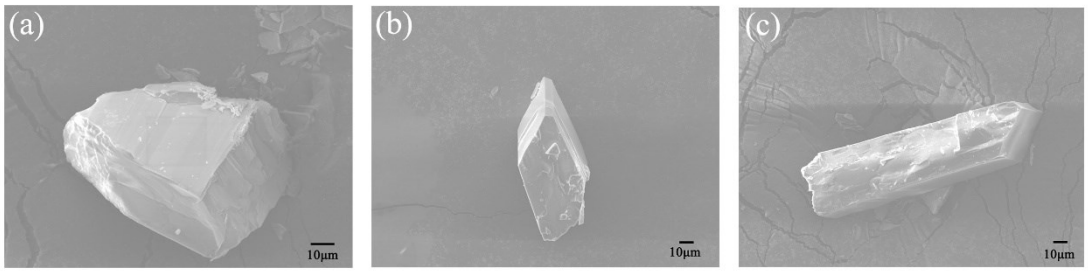

Figure S7. SEM images of **1**.

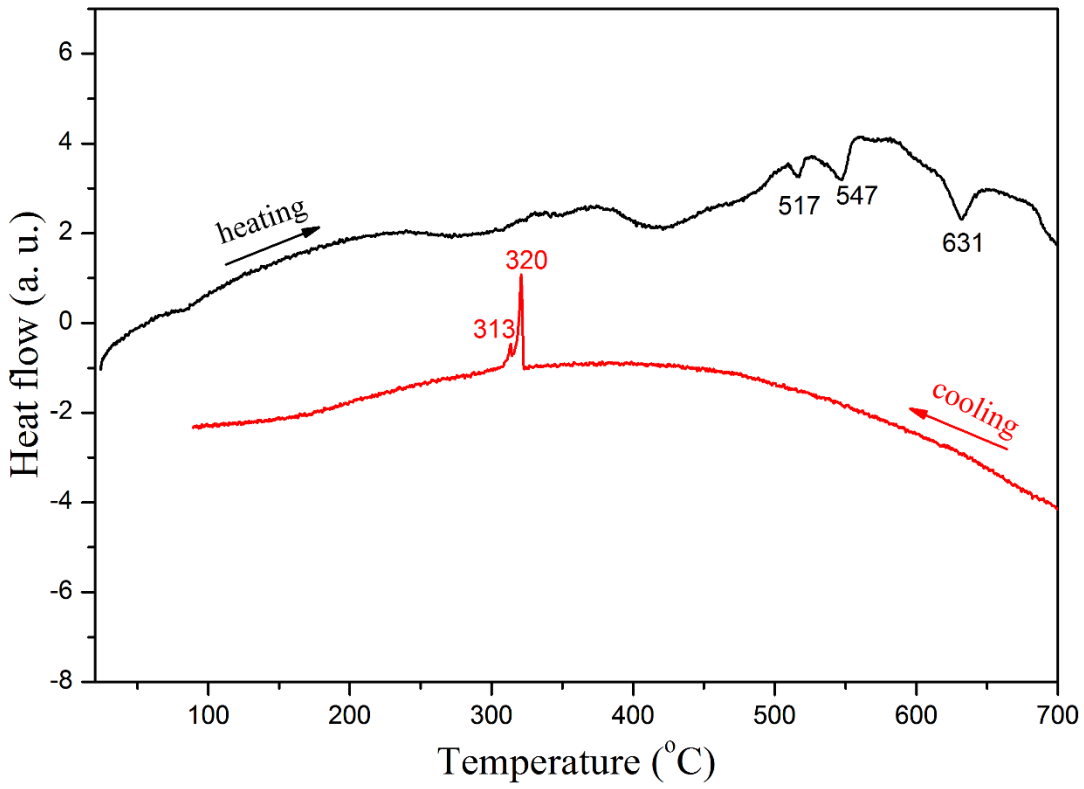

Figure S8. DSC curves for **1**.

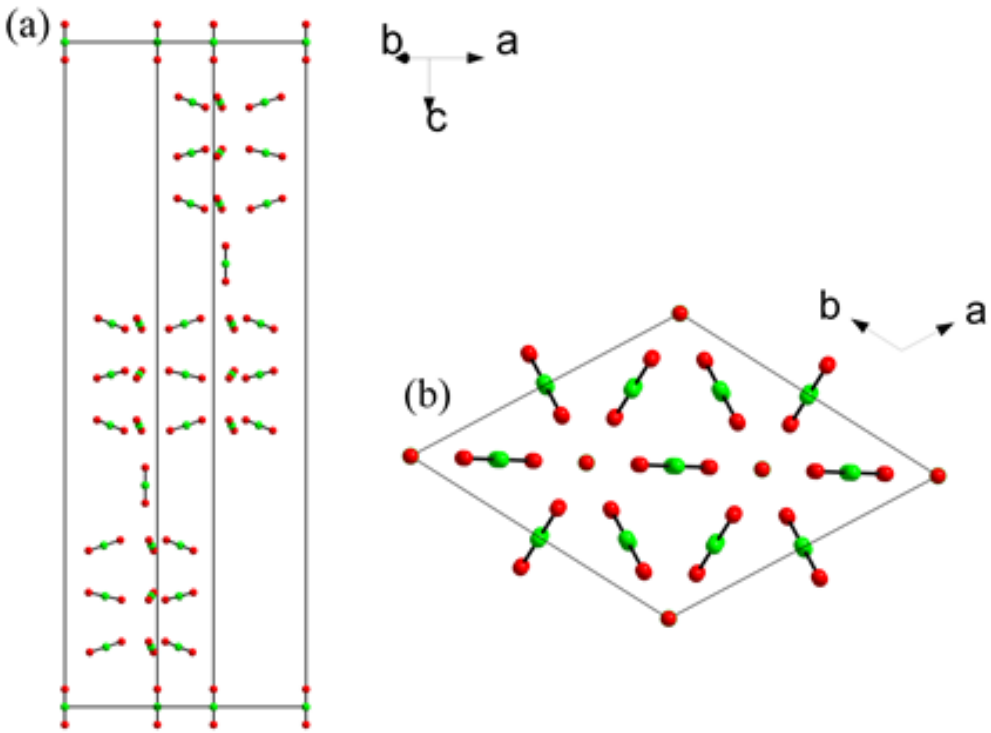

Figure S9. (a) Arrangement of CN_2 groups along *c* axis and (b) projection of the CN_2 units at *ab* plane.

Table S1. Crystal data and structural refinements for **1**.

Formula	$K_{12}Pb_{51}(CN_2)_{30}Cl_{54}$
M_r	14151.09
Crystal system	trigonal
Space group	$R\bar{3}m$
a, c (Å)	10.3072 (4), 45.528 (3)
α,γ (°)	90, 120
V/ Å^3	4188.8 (4)
Z	1
Crystal size (mm)	0.08 × 0.05 × 0.04
μ (mm−1)	52.23
*R*int	0.060
F(000)	*5928*
ρ_{calc} g/cm^3	*5.610*
Data/restraints/parameters	1122/0/78
Goodness-of-fit on F^2	1.162
Final R indexes [I>=2σ (I)]	R_1 = 0.0217, wR_2 = 0.0527
Final R indexes [all data]	R_1 = 0.0221, wR_2 = 0.0530

[a] $R_1=\sum||F_O|-|F_C|| / \sum|F_O|$ and $wR_2=\left[\sum\left[w\left(F_O^2-F_C^2\right)^2\right] / \sum\left[w\left(F_O^2\right)^2\right]\right]^{\frac{1}{2}}$ for $F_O^2 > 2\sigma\left(F_C^2\right)$

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **1**.

	x	y	z	U_{iso}*/U_{eq}
Pb1	0.13212 (2)	0.86788 (2)	0.20176 (2)	0.00803 (11)
Pb2	0.54138 (2)	0.08275 (4)	0.28049 (2)	0.01203 (11)
Pb3	0.000000	0.000000	0.12979 (2)	0.00848 (13)
Pb4	0.000000	0.000000	0.27164 (2)	0.01042 (14)
Pb5	0.166667	0.833333	0.333333	0.0086 (2)
K5	0.166667	0.833333	0.333333	0.0086 (2)
K1	0.333333	0.666667	0.23257 (6)	0.0036 (5)
Cl1	0.19359 (13)	0.80641 (13)	0.26972 (5)	0.0172 (5)
Cl2	0.48777 (14)	0.51223 (14)	0.20335 (5)	0.0209 (5)
Cl3	−0.14678 (15)	0.7064 (3)	0.31714 (5)	0.0199 (5)
C1	−0.166667	0.666667	0.166667	0.006 (2)
C2	0.8363 (5)	0.1637 (5)	0.24342 (16)	0.0076 (16)
C3	0.666667	0.333333	0.333333	0.012 (4)
N1	0.7697 (4)	0.2303 (4)	0.25105 (15)	0.0084 (14)
N2	−0.0988 (4)	0.8024 (8)	0.17183 (14)	0.0056 (13)
N3	−0.0984 (4)	0.8033 (8)	0.23505 (15)	0.0090 (14)
N4	0.666667	0.333333	0.3064 (3)	0.007 (2)

Table S3. Anisotropic displacement parameters (Å^2) for **1**.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.00605(14)	0.00605 (14)	0.01242 (18)	0.00336 (12)	−0.00037 (5)	0.00037 (5)
Pb2	0.01149(15)	0.00835 (18)	0.01519 (18)	0.00417 (9)	0.00075 (6)	0.00150 (11)
Pb3	0.00810(18)	0.00810 (18)	0.0092 (3)	0.00405 (9)	0.000	0.000
Pb4	0.01251(19)	0.01251 (19)	0.0062 (3)	0.00626 (9)	0.000	0.000
Pb5	0.0071 (3)	0.0071 (3)	0.0055 (4)	−0.0011 (4)	−0.00164 (18)	0.00164 (18)
K5	0.0071 (3)	0.0071 (3)	0.0055 (4)	−0.0011 (4)	−0.00164 (18)	0.00164 (18)
K1	0.0010 (8)	0.0010 (8)	0.0089 (13)	0.0005 (4)	0.000	0.000
Cl1	0.0173 (8)	0.0173 (8)	0.0179 (10)	0.0094 (9)	0.0014 (4)	−0.0014 (4)
Cl2	0.0159 (8)	0.0159 (8)	0.0334 (13)	0.0099 (10)	0.0045 (5)	−0.0045 (5)
Cl3	0.0190 (8)	0.0239 (12)	0.0186 (11)	0.0119 (6)	0.0032 (5)	0.0064 (9)
C1	0.007 (4)	0.009 (6)	0.004 (5)	0.005 (3)	0.002 (2)	0.004 (4)
C2	0.008 (3)	0.008 (3)	0.002 (3)	0.001 (4)	−0.0007 (15)	0.0007 (15)
C3	0.008 (6)	0.008 (6)	0.021 (12)	0.004 (3)	0.000	0.000
N1	0.007 (2)	0.007 (2)	0.011 (3)	0.004 (3)	−0.0016 (14)	0.0016 (14)
N2	0.007 (2)	0.003 (3)	0.006 (3)	0.0013 (17)	0.0001 (13)	0.000 (3)
N3	0.006 (2)	0.010 (4)	0.012 (3)	0.0051 (19)	−0.0006 (14)	−0.001 (3)
N4	0.009 (4)	0.009 (4)	0.004 (6)	0.0046 (18)	0.000	0.000

Table S4. Selected bond lengths and bond angles for **1**.

Pb1—N2^{i}	2.524 (4)	Pb5—Cl3^{viii}	2.9098 (12)
Pb1—N2	2.524 (4)	Pb5—Cl1	2.936 (2)
Pb1—N3^{i}	2.608 (4)	Pb5—Cl1^{vii}	2.936 (2)
Pb1—N3	2.608 (4)	K1—Cl1^{ix}	3.014 (3)
Pb2—N1	2.463 (4)	K1—Cl1^{v}	3.014 (3)
Pb2—N1^{ii}	2.464 (4)	K1—Cl1	3.014 (3)
Pb2—N4	2.529 (5)	K1—Cl2^{ix}	3.061 (3)
Pb3—N2^{v}	2.603 (7)	K1—Cl2^{v}	3.061 (3)
Pb3—N2^{vi}	2.603 (6)	K1—Cl2	3.061 (3)
Pb3—N2^{iv}	2.603 (6)	C1—N2^{x}	1.234 (7)
Pb4—N3^{iv}	2.420 (7)	C1—N2	1.234 (7)
Pb4—N3^{vi}	2.420 (7)	C2—N3^{iii}	1.228 (11)
Pb4—N3^{v}	2.420 (7)	C2—N1	1.238 (11)
Pb5—Cl3^{i}	2.9097 (12)	C3—N4	1.227 (12)
Pb5—Cl3	2.9098 (12)	C3—N4^{xi}	1.227 (12)
Pb5—Cl3^{vii}	2.9098 (12)		
N2^{i}—Pb1—N2	74.5 (3)	Pb2^{xv}—N1—Pb2	103.7 (3)
N2^{i}—Pb1—N3^{i}	68.20 (18)	C1—N2—Pb1^{xiv}	109.3 (2)
N2—Pb1—N3^{i}	109.5 (2)	C1—N2—Pb1	109.3 (2)
N2^{i}—Pb1—N3	109.5 (2)	Pb1^{xiv}—N2—Pb1	108.0 (2)
N2—Pb1—N3	68.21 (18)	C1—N2—Pb3^{xii}	121.7 (4)

N3^{i}—Pb1—N3	71.3 (3)	Pb1^{xiv}—N2—Pb3^{xii}	103.88 (18)
N1—Pb2—N1^{ii}	80.5 (3)	Pb1—N2—Pb3^{xii}	103.88 (18)
N1—Pb2—N4	77.3 (2)	C2^{xiii}—N3—Pb4^{xii}	118.4 (5)
N1^{ii}—Pb2—N4	77.3 (2)	C2^{xiii}—N3—Pb1	113.0 (3)
N2^{v}—Pb3—N2^{vi}	71.9 (2)	Pb4^{xii}—N3—Pb1	103.9 (2)
N2^{v}—Pb3—N2^{iv}	71.9 (2)	C2^{xiii}—N3—Pb1^{xiv}	113.0 (3)
N2^{vi}—Pb3—N2^{iv}	71.9 (2)	Pb4^{xii}—N3—Pb1^{xiv}	103.9 (2)
N3^{iv}—Pb4—N3^{vi}	77.9 (3)	Pb1—N3—Pb1^{xiv}	103.1 (2)
N3^{iv}—Pb4—N3^{v}	77.9 (3)	C3—N4—Pb2	117.8 (2)
N3^{vi}—Pb4—N3^{v}	77.9 (3)	C3—N4—Pb2^{xv}	117.8 (2)
N2^{x}—C1—N2	180.0	Pb2—N4—Pb2^{xv}	100.0 (3)
N3^{iii}—C2—N1	178.2 (8)	C3—N4—Pb2^{ii}	117.8 (2)
N4—C3—N4^{xi}	180.0	Pb2—N4—Pb2^{ii}	100.0 (3)
C2—N1—Pb2^{xv}	115.7 (3)	Pb2^{xv}—N4—Pb2^{ii}	100.0 (3)
C2—N1—Pb2	115.7 (3)		

Symmetry codes: (i) −*y*+1, *x*−*y*+2, *z*; (ii) −*x*+*y*+1, −*x*+1, *z*; (iii) −*x*+*y*, −*x*, *z*; (iv) *x*, *y*−1, *z*; (v) −*y*+1, *x*−*y*+1, *z*; (vi) −*x*+*y*−1, −*x*, *z*; (vii) −*x*+1/3, −*y*+5/3, −*z*+2/3; (viii) *y*−2/3, −*x*+*y*−1/3, −*z*+2/3; (ix) −*x*+*y*, −*x*+1, *z*; (x) −*x*−1/3, −*y*+4/3, −*z*+1/3; (xi) −*x*+4/3, −*y*+2/3, −*z*+2/3; (xii) *x*, *y*+1, *z*; (xiii) −*y*, *x*−*y*, *z*; (xiv) −*x*+*y*−1, −*x*+1, *z*; (xv) −*y*+1, *x*−*y*, *z*.

Table S5. A brief summary crystallographic data of reported metal carbodiimides.

Formula	Space	Unit cell dimensions		
	group	a/ Å	b/ Å	c/ Å
$MgCN_2$	*R* $\bar{3}$*m*	3.2734(1)	3.2734(1)	14.1282(5)
$CaCN_2$	*R* $\bar{3}$*m*	3.6900(3)	3.6900(3)	14.775(3)
$SrCN_2$	*Pnma*	12.410(2)	3.963(2)	5.389(2)
$BaCN_2$	*R* $\bar{3}$*c*	15.282(2)	15.282(2)	7.013(2)
$BaCN_2$	*I4/mcm*	6.0249(4)	6.0249(4)	7.1924(5)
$MnCN_2$	*R* $\bar{3}$*m*	3.3583(4)	3.3583(4)	14.347(2)
$FeCN_2$	*P6₃/mmc*	3.2689(2)	3.2689(2)	9.401 (1)
$CoCN_2$	*P6₃/mmc*	3.2129(4)	3.2129(4)	9.3902(2)
$NiCN_2$	*P6₃/mmc*	3.1533(8)	3.1533(8)	9.272(3)
$CuCN_2$	*Cmcm*	2.9921(1)	6.1782(1)	9.4003(2)
$PbCN_2$	*Pnma*	5.5566	3.8677	11.7350
$EuCN_2$	*Pnma*	12.3241(9)	3.9526(3)	5.3943(4)
$Hf(CN_2)_2$	*Pbcn*	9.4017(1)	7.9128(1)	5.8914(1)
$Eu_2(CN_2)_3$	*Pnma*	14.50285	3.86976	5.26743
$Cr_2(NCN)_3$	*R* $\bar{3}$*c*	5.4751(1)	5.4751(1)	27.9696(3)
$Lu_2(CN_2)_3$	*R* $\bar{3}$*c*	6.267(1)	6.267(1)	29.367(6)
$Yb_2(CN_2)_3$	*R* $\bar{3}$*c*	6.295(1)	6.295(1)	29.448(5)
$Tm_2(CN_2)_3$	*R* $\bar{3}$*c*	6.3434(2)	6.3434(2)	29.5486(8)

$RE_2(CN_2)_3$	*R32*	6.2732(8)-6.3393(7)	6.2732(8)-6.3393(7)	14.708(2)-14.723(3)
(RE=Tm-Lu)				
$RE_2(CN_2)_3$	*C2/m*	14.184(2)-14.853(2)	3.7471(3)-3.9907(6)	5.2051(5)-5.3243(9)
(RE=Y, Pr-Er)				
$SrZn(NCN)_2$	*Cmcm*	3.60940(2)	19.9329(1)	6.36842(3)
$LiAl(CN_2)_2$	*Pbcn*	9.174(3)	6.417(2)	5.391(2)
$Li_2Sn(CN_2)_3$	*Pnna*	5.7315(1)	9.5484(2)	9.9743(1)
$Na_2Sn(CN_2)_3$	*Pnna*	5.9323(1)	9.7745(1)	10.7278(1)
$Li_2Zr(CN_2)_3$	*R* $\bar{3}$*c*	5.7832(1)	5.7832(1)	28.9107(3)
$Li_2Hf(CN_2)_3$	*R* $\bar{3}$*c*	5.7759(1)	5.7759(1)	28.8025(2)
$LiY(CN_2)_2$	*Pbcn*	9.815(2)	6.992(2)	6.139(2)
$LiLa(CN_2)_2$	$P2_1/m$	5.424(2)	3.7916(7)	10.13(3)
$LaCN_2F$	*Cmcm*	3.8864(4)	8.7237(9)	7.8248(8)
$LiRE_2(CN_2)_2F_3$	*C2/c*	11.401(3)-11.662(1)	6.389(2)-6.6416(7)	8.322(3)-8.5551(9)
(RE=Ce-Gd)				
$LaSr_3(CN_2)_2F_5$	*I* $\bar{4}$*2m*	8.086(2)	8.086(2)	6.580(2)
$Eu_4(CN_2)_2F_5$	*P* $\bar{4}2_1c$	16.053(1)	16.053(1)	6.5150(6)
$Ba_4Mg(CN_2)_4F_2$	$P2_1/c$	8.351(2)	8.617(1)	8.442(2)
$La(CN_2)Cl$	$P2_1/m$	5.330(1)	4.0305(8)	7.545(1)
$Eu_2(CN_2)Cl_2$	*C2/m*	9.6200(17)	4.2299(7)	7.2224(13)
$Sr_2(CN_2)Cl_2$	*C2/m*	9.6225(9)	4.2508(4)	7.2498(6)

$LiSr_2(CN_2)Br$	*Fd* $\bar{3}$*m*	14.641	14.641	14.641
$LiEu_2(CN_2)Br_3$	*Fd* $\bar{3}$*m*	14.572	14.572	14.572
$LiSr_2(CN_2)I_3$	*Fd* $\bar{3}$*m*	15.231	15.231	15.231
$LiEu_4(CN_2)_3I_3$	*P6₃/mmc*	15.143(17)	15.143(17)	6.8232(10)
$Li_2RE_2Sr(CN_2)_5$ (Sm-Tb)	*C2/m*	13.692(5)-13.712(4)	3.6484(4)- 3.710(1)	11.417(2)-11.449(3)
$LiBa_2[Al(CN_2)_4]$	$P2_12_12_1$	6.843(1)	11.828(2)	11.857(2)
$LiSr_2[Al(CN_2)_4]$	*C2/c*	7.2311(1)	19.833(3)	7.2415(1)
$LiEu_2[Al(CN_2)_4]$	*C2/c*	7.224(2)	19.804(4)	7.226(2)
$LiSr_2[Ga(CN_2)_4]$.	*C2/c*	4.272(2)	19.857(4)	7.263(2)
$KRE[Si(CN_2)_4]$ (RE=La-Gd)	$P2_12_12$	9.277(6)-9.486(2)	7.522(3)-7.613(2)	6.649(4)-6.854(2)
$RbRE[Si(CN_2)_4]$ (RE=La-Lu, Y)	$I\bar{4}$	8.359(2)-8.645(2)	8.359(2)-8.645(2)	6.529(2)-6.851(2)
$CsRE[Si(CN_2)_4]$ (RE=La-Lu, Y)	$I\bar{4}$	8.359(2)-8.645(2)	8.359(2)-8.645(2)	6.529(2)-6.851(2)
K*RE*$[Ge(CN_2)_4]$ (RE=La-Gd)	$P2_12_12$	9.3103(5)- 9.4785(8)	7.5143(5)-7.6824(7)	6.7476(7)-6.9977(5)
Cs*RE*$[Ge(CN_2)_4]$ (RE=La-Gd)	$I\bar{4}$	8.5051(1)-8.6694(5)	8.5051(1)-8.6694(5)	6.7583(6)-6.9817(4)
$RbRE[Ge(CN_2)_4]$	$I\bar{4}$	8.4075(2)-8.5493(2)	8.4075(2)-8.5493(2)	6.7599(9)-6.9557(2)

(RE=La-Gd)

Reference

1 G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112-122.

2 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

3 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z Kristallogr*, 2005, **220**, 567-570.

4 F. Liang, L. Kang, X. Zhang, M.-H. Lee, Z. Lin and Y. Wu, *Cryst. Growth Des.*, 2017, **17**, 4015-4020.

5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

6 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207-8215.

7 D. Vanderbilt, *Phys. Rev. B: Condens. Matter*, 1990, **41**, 7892-7895.

8 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.