

## Diverse Structures of Metal – Organic Frameworks via a Side Chain Adjustment: Interpenetration and Gas Adsorption

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### Experimental Section

**Materials and Methods:** All chemicals and solvents except L1-L3 ligand were of reagent-grade quality from commercial sources and were used without further purification. IR spectra of the complexes were recorded on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of the sample in 300 mg of KBr) in the range of 400-4000  $\text{cm}^{-1}$ . C, H and N elemental analyses were performed with a Perkin Elmer 240C elemental analyzer. The as-synthesized complexes were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 700 K using a heating rate of 10  $\text{Kmin}^{-1}$  under a  $\text{N}_2$  atmosphere. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-K  $\alpha$  radiation (1.5418 Å), and the X-ray tube was operated at 40 kV and 40 mA. The gas sorption isotherms were measured by using a Micromeritics ASAP 2020 M + C surface area analyzer. Solid-state UV-vis diffuse reflectance spectra were obtained at room temperature using a Shimadzu UV-3600 double monochromator spectrophotometer, and  $\text{BaSO}_4$  was used as a 100% reflectance standard for all materials.

**Crystal Structure Determination:** Single crystal X-ray data of complexes 1–3 were collected at 293 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). The linear absorption coefficients, scattering factors for the atoms, and

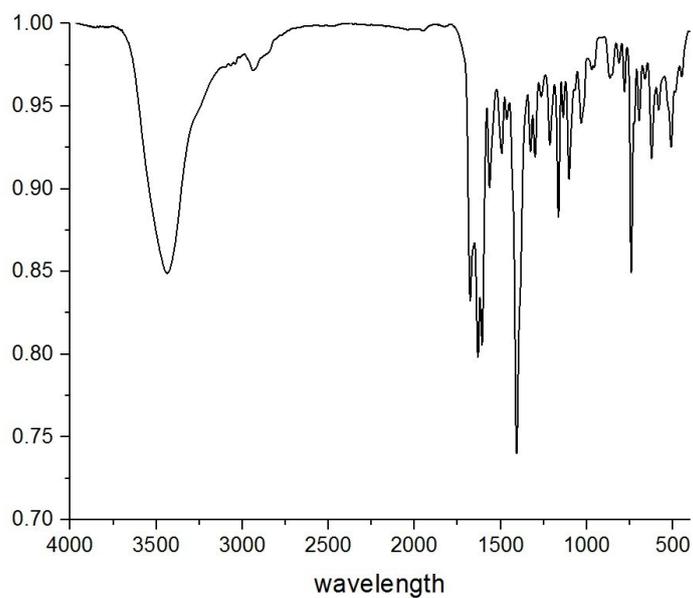
the anomalous dispersion corrections were referred to from the International Tables for X-ray Crystallography.<sup>1</sup> The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically using full-matrix least-squares procedures based on  $F^2$  values using SHELXTL (version 6.10) crystallographic software.<sup>2</sup> The H-atoms attached to carbon atoms were positioned geometrically and treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 1. Selective bond distances and angles are given in Table S1 (Supporting Information). The topological analysis and some diagrams were produced using the TOPOS program.<sup>3</sup>

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-3**.

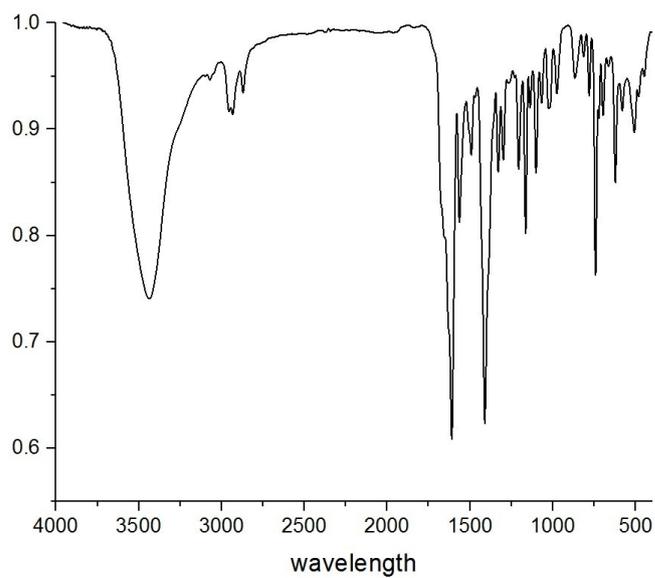
Complex 1			
Co(1)-O(6)#2	2.029(3)	Co(1)-O(3)#3	2.029(3)
Co(1)-O(7)#4	2.042(3)	Co(1)-N(1)	2.045(3)
Co(1)-O(2)	2.142(3)	O(6)#2-Co(1)-O(3)#3	92.19(14)
O(6)#2-Co(1)-O(7)#4	163.45(12)	O(3)#3-Co(1)-O(7)#4	92.97(15)
O(6)#2-Co(1)-N(1)	96.27(14)	O(3)#3-Co(1)-N(1)	106.59(15)
O(7)#4-Co(1)-N(1)	97.30(14)	O(6)#2-Co(1)-O(2)	86.58(13)
O(3)#3-Co(1)-O(2)	163.05(15)	O(7)#4-Co(1)-O(2)	83.90(13)
N(1)-Co(1)-O(2)	90.34(15)		
Complex 2			
Co(1)-O(3)	2.018(4)	Co(1)-O(2)#1	2.024(4)
Co(1)-O(1)#2	2.028(4)	Co(1)-N(1)	2.048(4)
Co(1)-O(4)#3	2.149(4)	O(3)-Co(1)-O(2)#1	92.21(17)
O(3)-Co(1)-O(1)#2	91.91(18)	O(2)#1-Co(1)-O(1)#2	162.50(14)
O(3)-Co(1)-N(1)	107.88(17)	O(2)#1-Co(1)-N(1)	97.36(17)
O(1)#2-Co(1)-N(1)	97.54(16)	O(3)-Co(1)-O(4)#3	162.89(18)
O(2)#1-Co(1)-O(4)#3	86.41(16)	O(1)#2-Co(1)-O(4)#3	84.67(16)
N(1)-Co(1)-O(4)#3	89.21(17)		

Complex 3			
Co(1)-O(24)#1	2.021(4)	Co(1)-O(23)#2	2.037(4)
Co(1)-O(20)#3	2.037(4)	Co(1)-O(19)	2.040(4)
Co(1)-N(1)	2.055(4)	O(24)#1-Co(1)-O(23)#2	163.42(16)
O(24)#1-Co(1)-O(20)#3	91.56(17)	O(23)#2-Co(1)-O(20)#3	86.84(17)
O(24)#1-Co(1)-O(19)	87.71(17)	O(23)#2-Co(1)-O(19)	89.20(18)
O(20)#3-Co(1)-O(19)	163.58(17)	O(24)#1-Co(1)-N(1)	99.73(16)
O(23)#2-Co(1)-N(1)	96.85(16)	O(20)#3-Co(1)-N(1)	96.34(17)
O(19)-Co(1)-N(1)	99.96(16)		

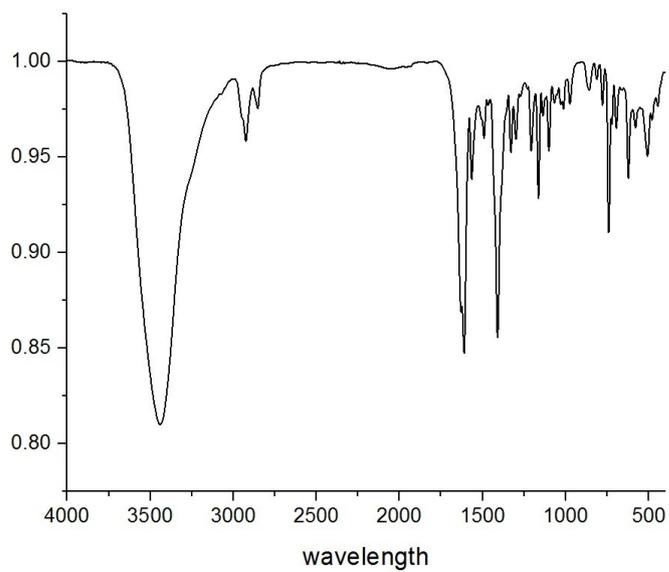
Symmetry codes: for **1**: #2 =  $x + 1/2, y - 1/2, z$ ; #3 =  $-x + 3/2, -y + 3/2, -z$ ; #4 =  $-x + 1, -y + 2, -z$ ; for **2**: #1 =  $-x, -y + 1, -z$ ; #2 =  $x - 1/2, y - 1/2, z$ ; #3 =  $-x - 1/2, -y + 1/2, -z$ ; for **3**: #1 =  $-x + 1, -y + 1, -z$ ; #2 =  $x, y + 1, z$ ; #3 =  $-x + 1, -y + 2, -z$ .



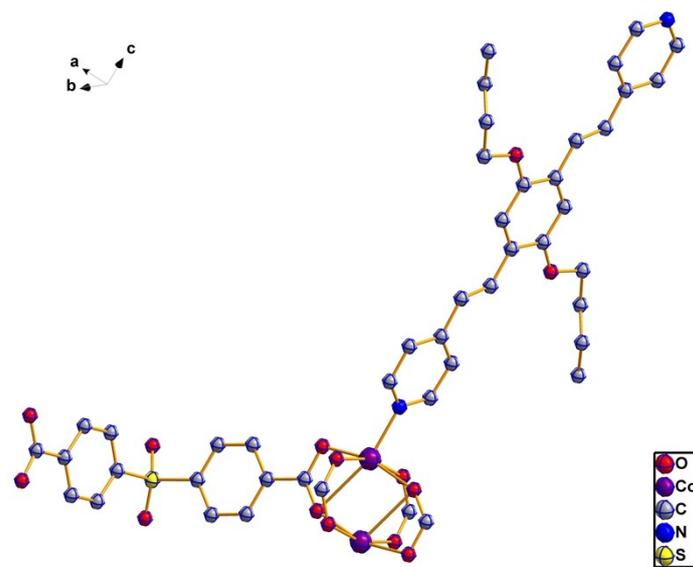
**Fig S1.** IR spectra of complex **1**



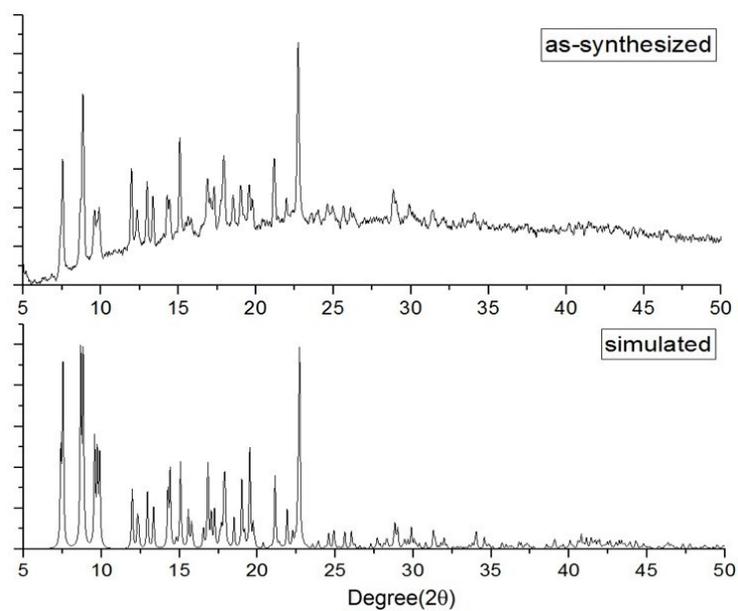
**Fig S2.** IR spectra of complex 2



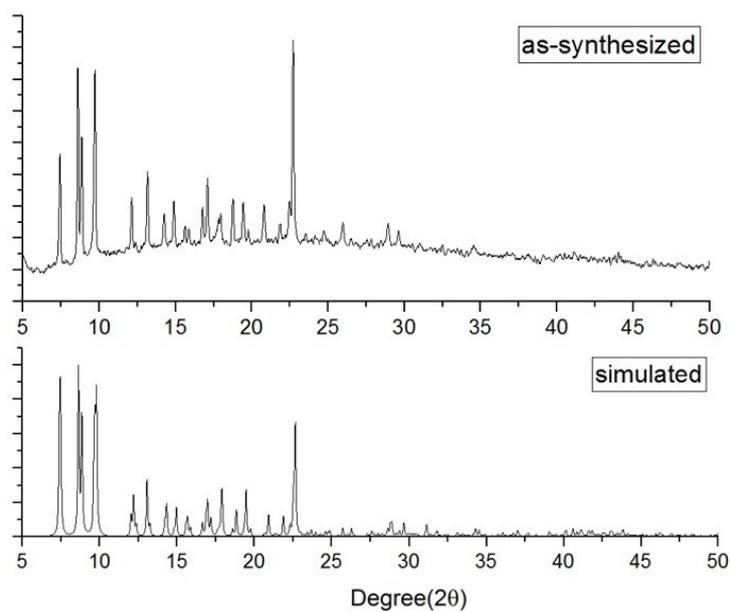
**Fig S3.** IR spectra of complex 3



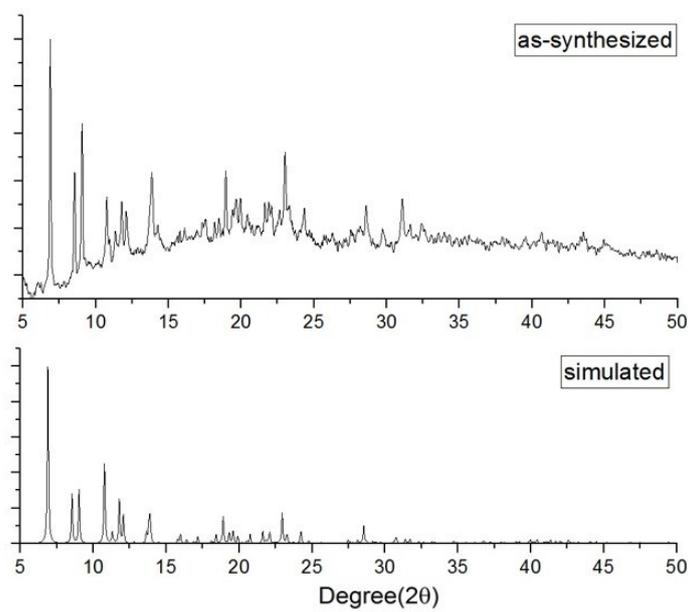
**Fig S4.** Coordination environment of the Co(II) ion in **2**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability).



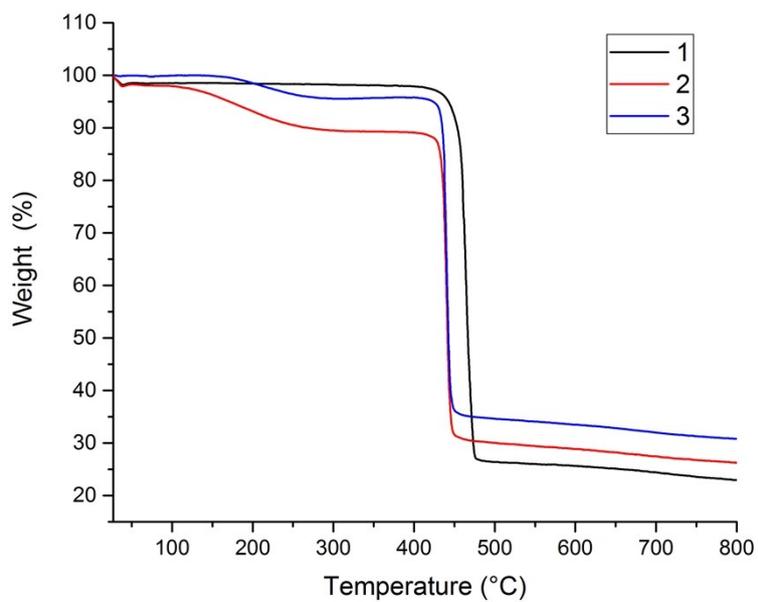
**Fig S5.** Powder X-ray diffraction patterns of complex **1**



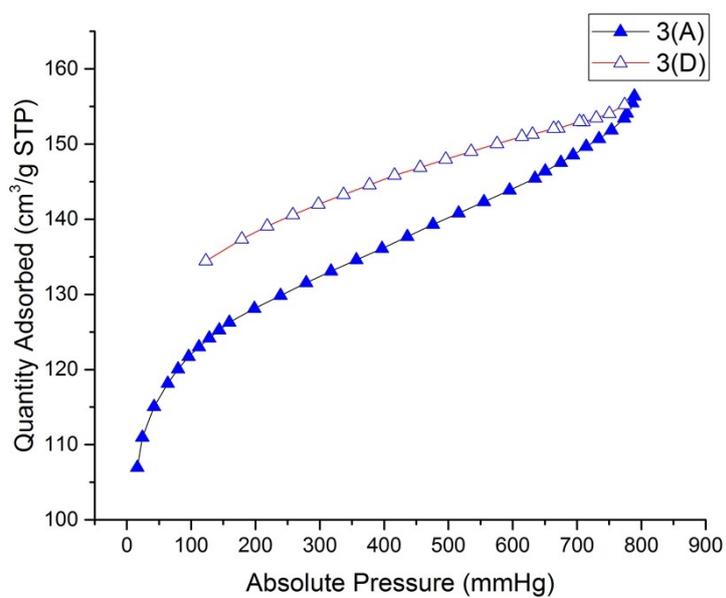
**Fig S6.** Powder X-ray diffraction patterns of complex 2



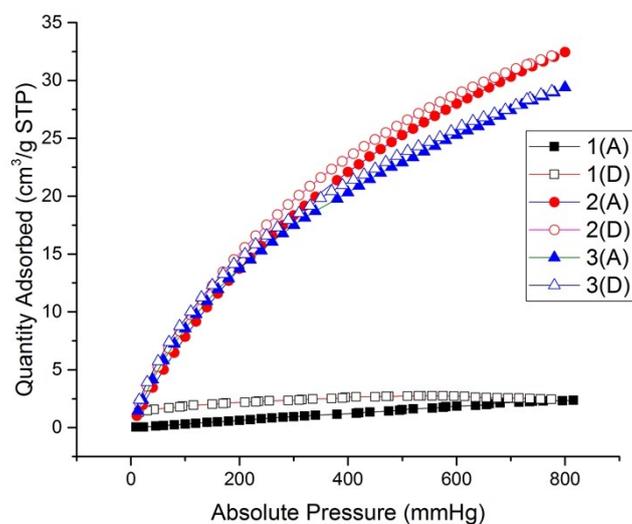
**Fig S7.** Powder X-ray diffraction patterns of complex 3



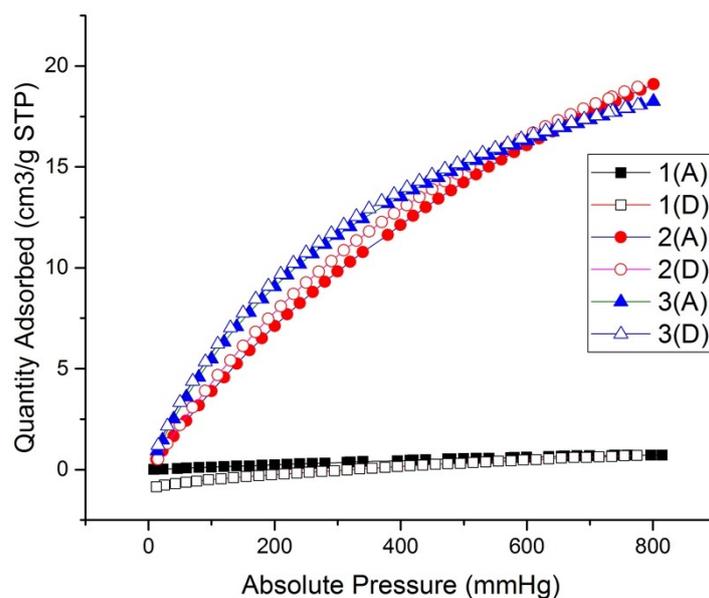
**Fig S8.** The TGA diagrams of complexes **1-3**.



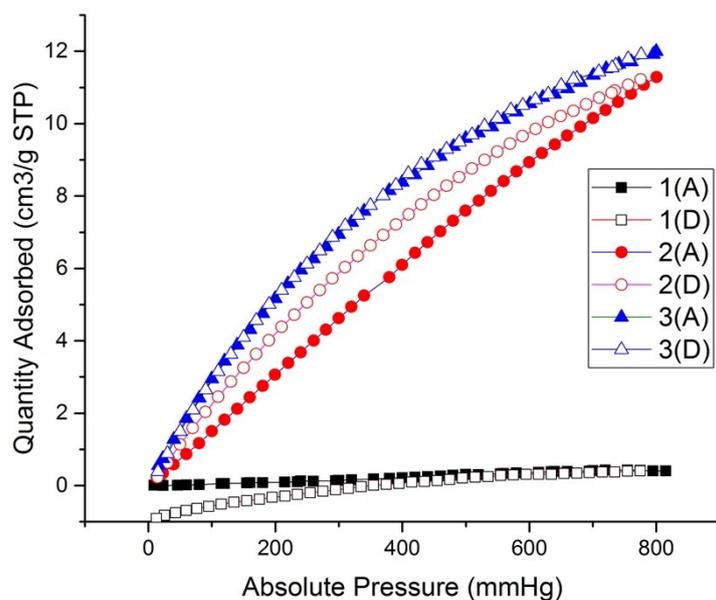
**Fig S9.** N<sub>2</sub> sorption isotherms for compounds **3** at 77 K. Filled symbols = adsorption; empty symbols = desorption.



**Fig S10.** CO<sub>2</sub> sorption isotherms for compounds **1-3** at 298 K. Filled symbols = adsorption; empty symbols = desorption.

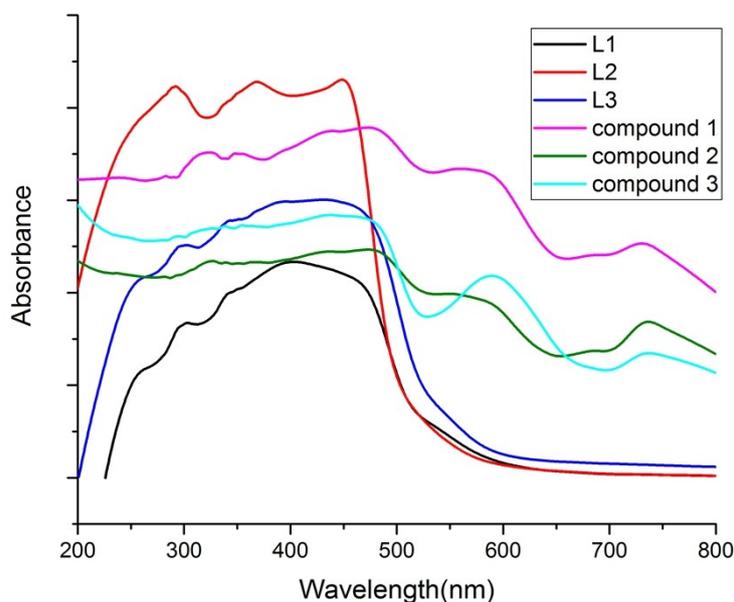


**Fig S11.** CH<sub>4</sub> sorption isotherms for compounds **1-3** at 273 K. Filled symbols = adsorption; empty symbols = desorption.



**Fig S12.** CH<sub>4</sub> sorption isotherms for compounds **1-3** at 298 K. Filled symbols = adsorption; empty symbols = desorption.

As can be seen in the UV – vis absorbance spectra in the Supporting Information (Fig S13), compounds **1 - 3** show intensive bands in the UV range at 200 - 330 nm; all of these peaks are due to the intraligand charge transfer transitions. In addition, for compounds **1 - 3**, we observe two additional peaks at 580 nm, and 730 nm.



**Fig S13.** UV-vis absorption spectra of ligands, and complexes **1-3**

## References

- 1 International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, England, 1952; Vol. III.
- 2 SMART (version 5.0), SAINT-Plus (version 6), SHELXTL (version 6.1), and SADABS (version 2.03); Bruker AXS Inc.: Madison, WI.
- 3 V. A. Blatov, A. P. Shevchenko, V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.