

**SUPPORTING
INFORMATION**

SUPPORTING INFORMATION

Crystallographic data for MOF-31-39

(123 pages)

Assembly of Metal-Organic Frameworks from Large Organic and Inorganic
Secondary Building Units: New Examples and Simplifying
Principles for Complex Structures

Jaheon Kim,[†] Banglin Chen,[‡] T. M. Reineke,[§] Hailian Li,[†] M. Eddaoudi,[†] D. B.
Moler,[†] M. O'Keeffe,[†] and O. M. Yaghi*,[†]

Materials Design and Discovery Group, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604.

Zn(ADC)₂•(HTEA)₂ (MOF-31),
Cd(ATC)•[Cd(H₂O)₆](H₂O)₅ (MOF-32),
Zn₂(ATB)(H₂O)₄•(H₂O)₃(DMF)₃ (MOF-33),
Ni₂(ATC)(H₂O)₄•(H₂O)₄ (MOF-34),
Zn₂(ATC)•(C₂H₅OH)₂(H₂O)₂ (MOF-35),
Zn₂(MTB)(H₂O)₂•(DMF)₆(H₂O)₅ (MOF-36),
Zn₂(NDC)₃•[(HTEA)(DEF)(ClBz)]₂ (MOF-37),
Zn₃O(BTC)₂•(HTEA)₂ (MOF-38),
Zn₃O(HBTB)₂(H₂O)•(DMF)_{0.5}(H₂O)₃ (MOF-39).

(Abbreviations: HTEA, triethylammonium; DMF, N,N'-dimethylformamide; DEF, N,N'-diethylformamide; ClBz, chlorobenzene; ADC, acetylenedicarboxylate; BTC, benzenetricarboxylate; NDC, 2,6-naphthalene dicarboxylate; BTB, benzenetribenzoate; MTB, methanetetrabenoate; ATC, adamantanetetracarboxylate; ATB, adamantanetetrabenzoate).

Introduction

The compound crystallized in the cubic space group $Pn\bar{3}m$. Structure solution was difficult due to the fact that the adc ligands were highly disordered. Initial refinement was in $Pn\bar{3}$ in an attempt to reduce the amount of disorder. The attempt was not successful. Refinement in the centric space group had the same model with far fewer parameters.

The overall stoichiometry of the framework is $Zn(O_2C-C\equiv C-CO_2)_2$. Assuming that the carboxylic acid is completely deprotonated, this implies that there should be two molecules of triethylammonium cation per Zn center. The diffuse electron density in the cavities was modeled with two C and a N each given a fixed Bis of 25.0 \AA^2 and refined with positional and occupancy factor. The final electron density summation comes reasonably close to meeting the charge-balance requirement.

Each Zn is coordinated by only one oxygen of each of four carboxylic acid groups. The other oxygen is clearly situated well away from the Zn. This allows the Zn to achieve ideal tetrahedral coordination, at least locally, at the expense of almost total disorder of the ADC ligands. The acetylinic carbon is refined anisotropically on the threefold axis of the cell. The coordinated oxygen is refined isotropically only because anisotropic refinement did not produce a significant reduction in the R-value. Both of these atoms are on the crystallographic 3m axis. The non-coordinated oxygen is disordered over six positions around the axis as are the carboxylic acid carbons.

The framework consists of interlinked three-dimensional structures which leave large channels running through the structure (see figure). These channels are where the diffuse electron density (not shown) resides.

Given the horrid aspects of the structure, it actually refined to a reasonable set of agreement factors. The usual files and such are attached.

Experimental

Data Collection

A colorless polyhedral crystal of $ZnO_8N_2C_{16}H_{30}$ having approximate dimensions of $0.14 \times 0.14 \times 0.19$ mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART¹⁰ CCD area detector with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 1134 reflections in the range $3.00 < 2\theta < 45.00^\circ$ corresponded to a primitive cubic cell (laue class: $m\bar{3}m$) with dimensions:

$$a = 10.8212(13) \text{ \AA}$$

$$V = 1267.1(3) \text{ \AA}^3$$

For $Z = 2$ and F.W. = 443.80, the calculated density is 1.16 g/cm^3 . Based on the systematic absences of:

$$0kl: k+l \neq 2n$$

and the successful solution and refinement of the structure, the space group was determined to be:

$$Pn\bar{3}m (\#224)$$

The data were collected at a temperature of $-115 \pm 1^\circ\text{C}$. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 20.0 seconds per frame.

Data Reduction

Data were integrated by the program SAINT¹¹ to a maximum 2θ value of 46.1° . The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP¹². An empirical absorption correction based on comparison of redundant and equivalent reflections as applied using SADABS¹³ ($\text{Tmax}=0.89$, $\text{Tmin}=0.73$).

Structure Solution and Refinement

The structure was solved by direct methods¹ and volume information (See introduction). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The final cycle of full-matrix least-squares refinement³ was based on 130 observed reflections ($I > 2.50\sigma(I)$) and 24 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.055$$

$$R_w = \sqrt{(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)} = 0.065$$

The standard deviation of an observation of unit weight⁴ was 3.11. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.18 and $-0.28 \text{ e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbel⁸. All calculations were performed using the teXsan⁹ crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A. (1993). *J. Appl. Cryst.*, 26, 343.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

$$\text{Function minimized: } \Sigma w(|F_o| - |F_c|)^2$$

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

(10) SMART: Area-Detector Software Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (1995-99)

(11) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(12) XPREP:(v 5.03) Part of the SHELXTL Crystal Structure Determination Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(13) SADABS: Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

*EXPERIMENTAL DETAILS***A. Crystal Data**

Empirical Formula	ZnO ₈ N ₂ C ₁₆ H ₃₀
Formula Weight	443.80
Crystal Color, Habit	colorless, polyhedral
Crystal Dimensions	0.14 X 0.14 X 0.19 mm
Crystal System	cubic
Lattice Type	Primitive
Lattice Parameters	$a = 10.8212(13)\text{\AA}$ $V = 1267.1(3) \text{\AA}^3$
Space Group	Pn\bar{3}m (#224)
Z value	2
D _{calc}	1.163 g/cm ³
F ₀₀₀	468.00
$\mu(\text{MoK}\alpha)$	23.73 cm ⁻¹

B. Intensity Measurements

Diffractometer	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{\AA}$) graphite monochromated
Detector Position	60.00 mm
Exposure Time	20.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
$2\theta_{max}$	46.1°
No. of Reflections Measured	Total: 5111 Unique: 108 ($R_{int} = 0.027$)

Corrections

Lorentz-polarization
Absorption (Tmax = 0.89, Tmin = 0.73)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(F_o - F_c)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(F_o)} = [\sigma_c^2(F_o) + \frac{\rho^2}{4} F_o^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.50\sigma(I)$)	130
No. Variables	24
Reflection/Parameter Ratio	5.42
Residuals: R; Rw; Rall	0.055 ; 0.065; 0.082
Goodness of Fit Indicator	3.11
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.18 e^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.28 e^-/\text{\AA}^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq} and occupancy

atom	x	y	z	B_{eq}	occ
Zn(1)	0.2500	0.2500	0.2500	5.90(11)	1/24
O(1)	0.1476(8)	0.1476	0.1476	10.3(4)	1/16
O(2)	0.246(4)	0.107(2)	0.022(3)	12.6(9)	1/16
N(1)	0.5000	-0.064(3)	0.0636	25.0000	0.155(8)
C(1)	0.166(6)	0.089(4)	0.0887	5.6(12)	1/12
C(2)	0.0286(9)	0.0286	0.0286	12.94(11)	1/16
C(3)	0.132(6)	0.1322	0.0361	11.0(19)	1/12
C(4)	0.438(5)	-0.172(6)	0.173(6)	25.0000	0.29(2)
C(5)	0.28(2)	-0.1990	0.2157	25.0000	0.056(14)

$$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(2)	0.164(9)	0.1639	0.1639	-0.045(7)	-0.0448	-0.0448

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
ZN1	O1	1.919(15)	ZN1	O1	1.919(15)
ZN1	O1	1.919(15)	ZN1	O1	1.919(15)
O1	C1	0.92(5)	O1	C1	0.92(5)
O1	C1	0.92(5)	O1	C3	1.23(2)
O1	C3	1.23(2)	O1	C3	1.23(2)
O2	O2	1.30(5)	O2	C1	1.14(5)
O2	C3	1.27(5)	N1	N1	1.68(8)
N1	N1	1.68(8)	N1	N1	0.97(5)
N1	N1	0.97(5)	N1	C4	1.79(5)
N1	C4	1.79(5)	C1	C1	1.19(10)
C1	C1	1.19(10)	C1	C2	1.75(6)
C1	C3	0.83(3)	C1	C3	1.56(6)
C1	C3	0.83(3)	C2	C2	1.07(3)
C2	C3	1.59(8)	C2	C3	1.59(8)
C2	C3	1.59(8)	C3	C3	1.47(9)
C3	C3	1.47(9)	C4	C4	1.69(11)
C4	C4	1.34(10)	C4	C5	1.8(2)
C5	C5	1.0(6)	C5	C5	1.3(2)
C5	C5	1.3(2)			

Table 4. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
O1	ZN1	O1	109.471(7)	O1	ZN1	O1	109.471(3)
O1	ZN1	O1	109.471(3)	O1	ZN1	O1	109.471(3)
O1	ZN1	O1	109.471(3)	O1	ZN1	O1	109.471(7)
ZN1	O1	C1	132.0(41)	ZN1	O1	C1	132.0(41)
ZN1	O1	C1	132.0(41)	ZN1	O1	C3	136.3(41)
ZN1	O1	C3	136.3(41)	ZN1	O1	C3	136.3(41)
C1	O1	C1	80.1(62)	C1	O1	C1	80.1(62)
C1	O1	C3	42.2(17)	C1	O1	C3	91.7(44)
C1	O1	C3	42.2(17)	C1	O1	C1	80.1(62)
C1	O1	C3	42.2(17)	C1	O1	C3	42.2(17)
C1	O1	C3	91.7(44)	C1	O1	C3	91.7(44)
C1	O1	C3	42.2(17)	C1	O1	C3	42.2(17)
C3	O1	C3	73.4(64)	C3	O1	C3	73.4(64)
C3	O1	C3	73.4(64)	O2	O2	C1	55.3(24)
O2	O2	C3	93.9(27)	C1	O2	C3	39.7(16)
N1	N1	N1	60.000(4)	N1	N1	N1	90.000(4)
N1	N1	N1	30.0	N1	N1	C4	130.6(16)
N1	N1	C4	162.7(24)	N1	N1	N1	30.0
N1	N1	N1	90.000(4)	N1	N1	C4	162.7(24)
N1	N1	C4	130.6(16)	N1	N1	N1	120.000(4)
N1	N1	C4	136.6(20)	N1	N1	C4	101.6(18)
N1	N1	C4	101.6(18)	N1	N1	C4	136.6(20)
C4	N1	C4	44.0(29)	O1	C1	O2	118.8(52)
O1	C1	O2	118.8(52)	O1	C1	C1	49.9(31)
O1	C1	C1	49.9(31)	O1	C1	C2	108.9(51)
O1	C1	C3	89.1(47)	O1	C1	C3	52.0(38)
O1	C1	C3	89.1(47)	O2	C1	O2	69.5(48)
O2	C1	C1	114.3(22)	O2	C1	C1	168.7(33)
O2	C1	C2	118.3(43)	O2	C1	C3	78.7(42)
O2	C1	C3	145.2(22)	O2	C1	C3	144.9(59)
O2	C1	C1	168.7(33)	O2	C1	C1	114.3(22)
O2	C1	C2	118.3(43)	O2	C1	C3	144.9(59)
O2	C1	C3	145.2(22)	O2	C1	C3	78.7(42)
C1	C1	C1	60.000(4)	C1	C1	C2	70.1(15)
C1	C1	C3	44.0(36)	C1	C1	C3	31.5(13)
C1	C1	C3	99.8(51)	C1	C1	C2	70.1(15)
C1	C1	C3	99.8(51)	C1	C1	C3	31.5(13)
C1	C1	C3	44.0(36)	C2	C1	C3	64.8(89)
C2	C1	C3	56.9(43)	C2	C1	C3	64.8(89)
C3	C1	C3	68.3(61)	C3	C1	C3	126(17)

Table 4. Bond Angles($^{\circ}$) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C3	C1	C3	68.3(61)	C1	C2	C1	39.7(29)
C1	C2	C1	39.7(29)	C1	C2	C2	156.9(17)
C1	C2	C3	28.1(5)	C1	C2	C3	55.5(18)
C1	C2	C3	28.1(5)	C1	C2	C1	39.7(29)
C1	C2	C2	156.9(17)	C1	C2	C3	28.1(5)
C1	C2	C3	28.1(5)	C1	C2	C3	55.5(18)
C1	C2	C2	156.9(17)	C1	C2	C3	55.5(18)
C1	C2	C3	28.1(5)	C1	C2	C3	28.1(5)
C2	C2	C3	147.6(4)	C2	C2	C3	147.6(4)
C2	C2	C3	147.6(4)	C3	C2	C3	55.2(6)
C3	C2	C3	55.2(6)	C3	C2	C3	55.2(6)
O1	C3	O2	90.7(30)	O1	C3	O2	90.7(30)
O1	C3	C1	48.7(39)	O1	C3	C1	48.7(39)
O1	C3	C1	36.3(17)	O1	C3	C2	104.0(43)
O1	C3	C3	53.3(32)	O1	C3	C3	53.3(32)
O2	C3	O2	113.7(72)	O2	C3	C1	61.6(45)
O2	C3	C1	136.8(83)	O2	C3	C1	109.5(15)
O2	C3	C2	121.8(35)	O2	C3	C3	140.2(16)
O2	C3	C3	86.1(27)	O2	C3	C1	136.8(83)
O2	C3	C1	61.6(45)	O2	C3	C1	109.5(15)
O2	C3	C2	121.8(35)	O2	C3	C3	86.1(27)
O2	C3	C3	140.2(16)	C1	C3	C1	92.1(71)
C1	C3	C1	48.7(44)	C1	C3	C2	87.1(91)
C1	C3	C3	80.2(51)	C1	C3	C3	27.2(83)
C1	C3	C1	48.7(44)	C1	C3	C2	87.1(91)
C1	C3	C3	27.2(83)	C1	C3	C3	80.2(51)
C1	C3	C2	67.7(47)	C1	C3	C3	31.5(13)
C1	C3	C3	31.5(13)	C2	C3	C3	62.4(3)
C2	C3	C3	62.4(3)	C3	C3	C3	60.000(2)
N1	C4	C4	78.4(18)	N1	C4	C4	68.0(14)
N1	C4	C5	129.8(38)	C4	C4	C4	134.6(45)
C4	C4	C5	61.1(52)	C4	C4	C5	161.8(42)
C4	C5	C4	58(10)	C4	C5	C5	149.2(57)
C4	C5	C5	106.7(15)	C4	C5	C5	132(16)
C4	C5	C5	149.2(57)	C4	C5	C5	132(16)
C4	C5	C5	106.7(15)	C5	C5	C5	66.8(92)
C5	C5	C5	66.8(92)	C5	C5	C5	46(18)

Table 5. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
ZN1	C1	2.63(6)	6	ZN1	C1	2.63(6)	7
ZN1	C1	2.63(6)	8	ZN1	C1	2.63(6)	10
ZN1	C1	2.63(6)	11	ZN1	C1	2.63(6)	12
ZN1	O2	2.91(3)	6	ZN1	O2	2.91(3)	7
ZN1	O2	2.91(3)	8	ZN1	O2	2.91(3)	10
ZN1	O2	2.91(3)	11	ZN1	O2	2.91(3)	12
ZN1	O2	2.91(3)	14	ZN1	O2	2.91(3)	15
ZN1	O2	2.91(3)	16	ZN1	O2	2.91(3)	17
ZN1	O2	2.91(3)	18	ZN1	O2	2.91(3)	19
ZN1	O2	2.91(3)	20	ZN1	O2	2.91(3)	21
ZN1	O2	2.91(3)	22	ZN1	O2	2.91(3)	23
ZN1	O2	2.91(3)	24	ZN1	C3	2.93(5)	6
ZN1	C3	2.93(5)	7	ZN1	C3	2.93(5)	8
ZN1	C3	2.93(5)	10	ZN1	C3	2.93(5)	11
ZN1	C3	2.93(5)	12	O1	O2	1.78(3)	17
O1	O2	1.78(3)	21	O1	O2	3.20(3)	6
O1	O2	3.20(3)	11	O1	O2	3.20(3)	15
O1	O2	3.20(3)	20	O1	O2	3.20(3)	22
O1	C1	3.55(5)	6	O1	C1	3.55(5)	8
O1	C1	3.55(5)	10	O1	C1	3.55(5)	11
O1	C3	3.58(8)	6	O1	C3	3.58(8)	11
O2	O2	2.13(7)	17	O2	O2	2.25(7)	20
O2	C4	2.33(7)	8	O2	N1	2.54(4)	8
O2	C5	2.70(6)	8	O2	N1	2.78(3)	23
O2	C4	2.93(7)	54544	O2	N1	2.94(4)	13
O2	C4	3.04(6)	13	O2	C5	3.09(15)	5
O2	O2	3.11(6)	8	O2	O2	3.11(6)	11
O2	C1	3.12(6)	8	O2	C4	3.17(7)	23
O2	C4	3.29(7)	55435	O2	N1	3.34(5)	1
O2	O2	3.42(7)	21	O2	N1	3.48(5)	11
O2	O2	3.55(7)	23	N1	N1	1.95(10)	13
N1	C4	2.21(4)	54532	N1	C4	2.59(6)	55435
N1	C4	3.16(7)	54544	N1	C5	3.2(3)	54532
N1	C4	3.44(8)	55447	N1	C1	3.49(6)	11
N1	C1	3.49(6)	54532	C1	C4	3.33(9)	8
C1	C4	3.33(9)	23	C2	C3	2.56(9)	29

Table 5. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	ADC	atom	atom	distance	ADC
C2	C3	2.56(9)	33	C3	C5	3.16(8)	5
C3	C5	3.16(8)	8	C3	C4	3.18(8)	8
C3	C4	3.18(8)	16	C4	C4	2.73(8)	64538
C4	C4	2.81(7)	54532	C4	C4	2.81(7)	55435
C4	C5	3.1(3)	54532	C4	C5	3.53(13)	31
C4	C4	3.54(9)	54522	C4	C4	3.54(9)	54524

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one-digit numbers and one two-digit number: TA (first digit) + TB (second digit) + TC (third digit) + SN (last two digits). TA, TB and TC are the crystal lattice translation digits along cell edges a, b and c. A translation digit of 5 indicates the origin unit cell. If TA = 4, this indicates a translation of one unit cell length along the a-axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus ± 4 lattice translations from the origin (TA=5, TB=5, TC=5) can be represented.

The SN, or symmetry operator number, refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always 55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of the atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through symmetry operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (eg. cation and anion) that reside in the same asymmetric unit.

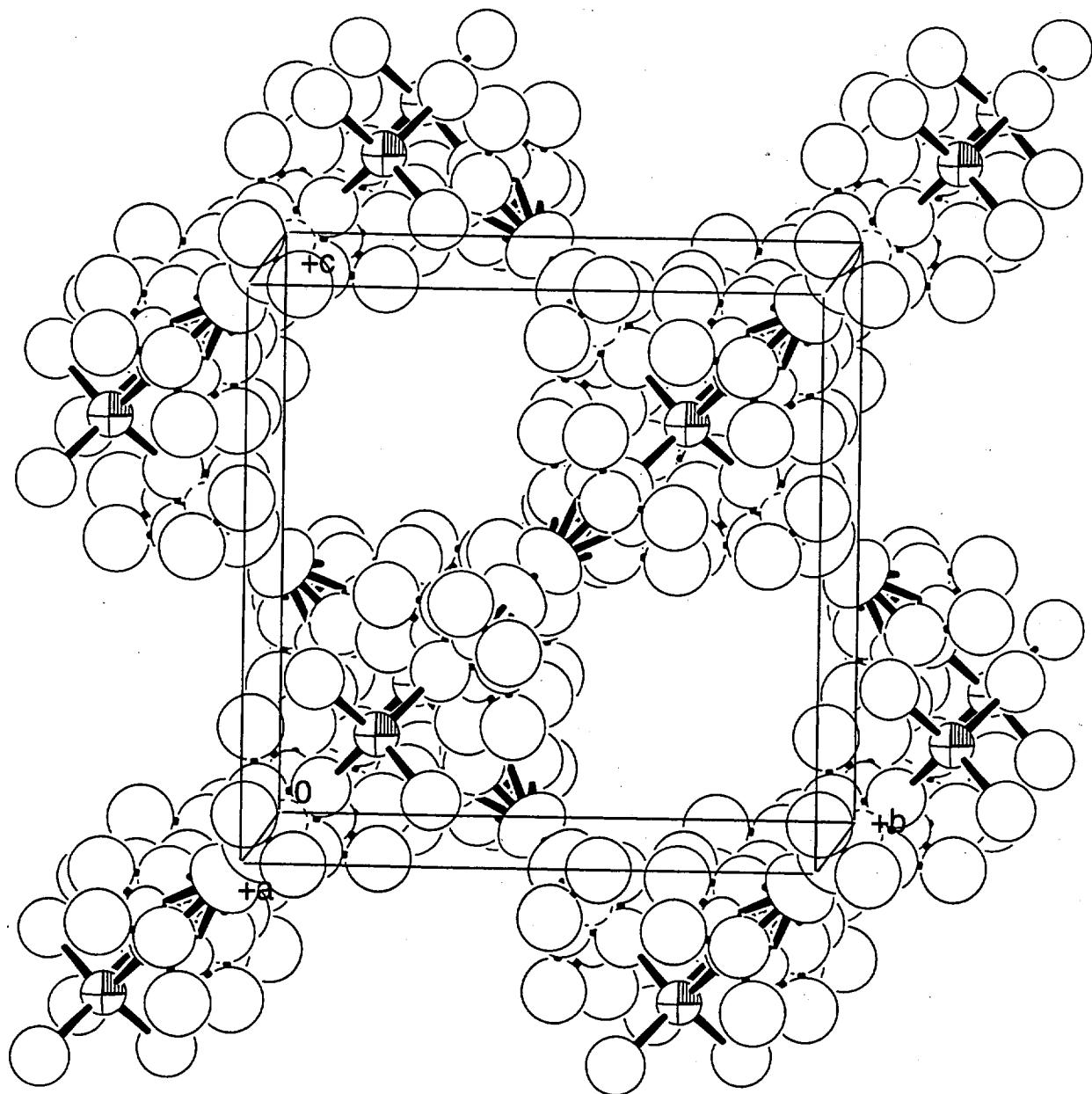
Symmetry Operators:

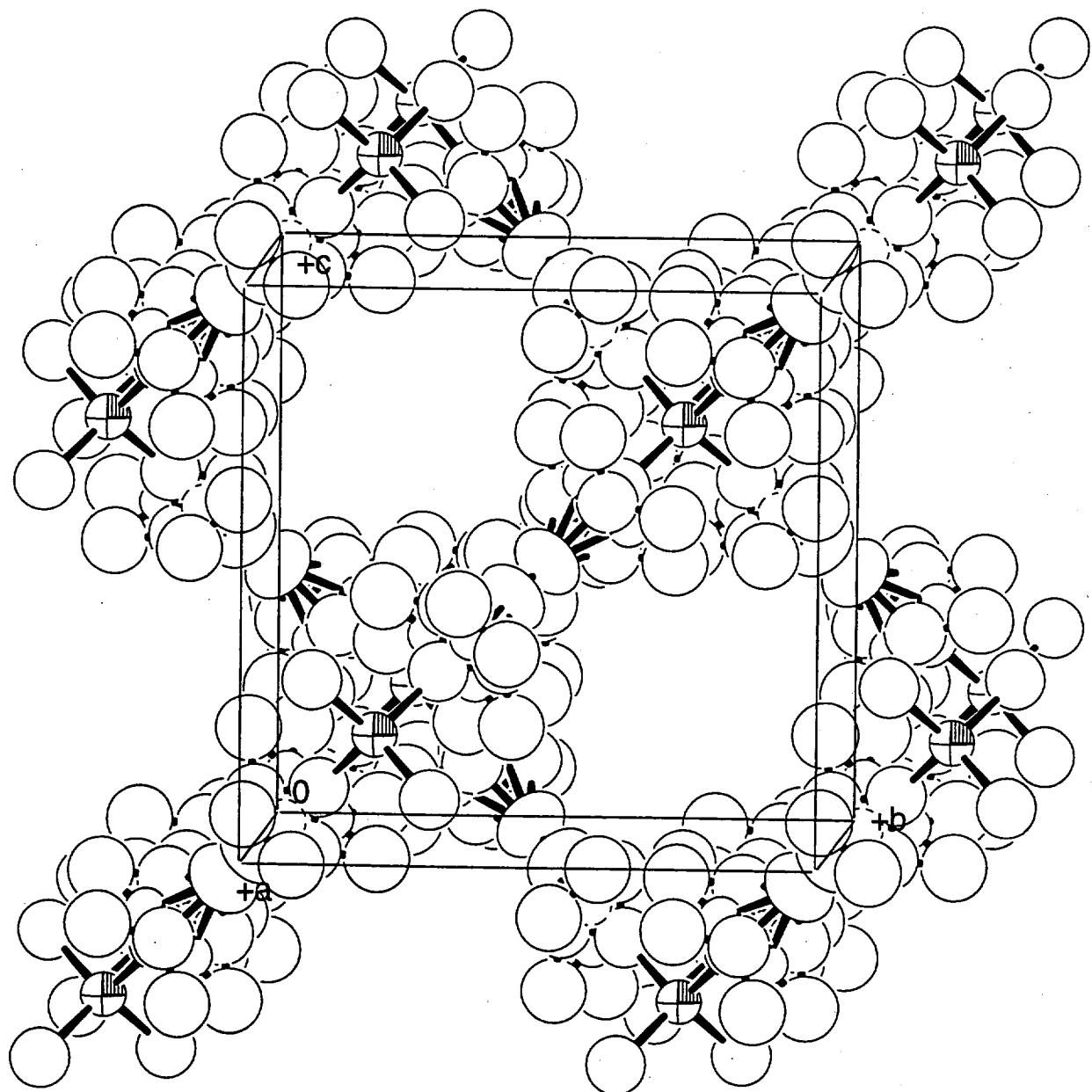
(1)	X,	Y,	Z	(2)	X,	1/2-Y,	1/2-Z
(3)	1/2-X,	Y,	1/2-Z	(4)	1/2-X,	1/2-Y,	Z
(5)	Z,	X,	Y	(6)	Z,	1/2-X,	1/2-Y
(7)	1/2-Z,	X,	1/2-Y	(8)	1/2-Z,	1/2-X,	Y
(9)	Y,	Z,	X	(10)	Y,	1/2-Z,	1/2-X
(11)	1/2-Y,	Z,	1/2-X	(12)	1/2-Y,	1/2-Z,	X
(13)	X,	Z,	Y	(14)	X,	1/2-Z,	1/2-Y
(15)	1/2-X,	Z,	1/2-Y	(16)	1/2-X,	1/2-Z,	Y
(17)	Y,	X,	Z	(18)	Y,	1/2-X,	1/2-Z
(19)	1/2-Y,	X,	1/2-Z	(20)	1/2-Y,	1/2-X,	Z
(21)	Z,	Y,	X	(22)	Z,	1/2-Y,	1/2-X
(23)	1/2-Z,	Y,	1/2-X	(24)	1/2-Z,	1/2-Y,	X
(25)	-X,	-Y,	-Z	(26)	-X,	1/2+Y,	1/2+Z
(27)	1/2+X,	-Y,	1/2+Z	(28)	1/2+X,	1/2+Y,	-Z
(29)	-Z,	-X,	-Y	(30)	-Z,	1/2+X,	1/2+Y
(31)	1/2+Z,	-X,	1/2+Y	(32)	1/2+Z,	1/2+X,	-Y
(33)	-Y,	-Z,	-X	(34)	-Y,	1/2+Z,	1/2+X
(35)	1/2+Y,	-Z,	1/2+X	(36)	1/2+Y,	1/2+Z,	-X
(37)	-X,	-Z,	-Y	(38)	-X,	1/2+Z,	1/2+Y
(39)	1/2+X,	-Z,	1/2+Y	(40)	1/2+X,	1/2+Z,	-Y
(41)	-Y,	-X,	-Z	(42)	-Y,	1/2+X,	1/2+Z

(43) $1/2+Y, -X,$ $1/2+Z$
(45) $-Z, -Y,$ $-X$
(47) $1/2+Z, -Y,$ $1/2+X$

(44) $1/2+Y, 1/2+X,$ $-Z$
(46) $-Z, 1/2+Y,$ $1/2+X$
(48) $1/2+Z, 1/2+Y,$ $-X$

	10 Fo	VB 10 Fc	For Zn(adc)2 (ETC3NH)2 at -115
h	k	l	Fo Fc sigF h k
1	1	1	949 1025 15 6 2
1	1	0	195 195 3 6 2
1	1	0	123 118 3 6 3
2	2	0	575 546 9 6 3
2	1	1	243 248 4 7 7
2	1	1	72 70 2 7 7
2	2	0	205 210 4 7 7
2	2	0	820 789 13 6 3
2	2	0	3 3 179 180 3 8 0
2	2	1	0 0 218 217 5 9 5
2	2	1	621 566 10 6 4
2	2	1	0 0 1 1 180 184 3 9 5
2	2	2	219 229 4 6 4
2	2	2	1 1 23 40 5* 8 2 0
2	2	2	0 0 163 154 3 9 5 5
3	3	1	1 1 169 161 3 6 4
3	3	1	2 3 30 2 6 4 3 9 6*
3	3	1	3 4 34 30 2 6 4 3 9 6*
3	3	2	1 3 385 405 6 6 4 4 134 139 3 8 3 1
3	3	2	2 3 2 2 249 252 4 6 5 1 202 212 3 8 3 2
3	3	2	3 3 3 2 275 272 5 6 6 0 138 152 4 8 4 3 0
3	3	3	3 3 1 233 234 4 6 6 1 0 28 11* 8 4 4 77 89 4 10 0
3	3	3	3 3 2 195 204 3 6 6 2 156 152 3 8 5 1 100 104 3 10 1
3	3	4	4 4 2 54 58 2 6 6 3 15 7 11* 8 5 2 0 1 11* 10 2
3	3	4	4 4 2 490 523 8 6 6 4 95 99 3 8 5 3 78 88 3 10 2
3	3	4	4 4 3 1 426 404 7 6 6 5 0 13 12* 8 5 4 25 3 8* 10 2
3	3	4	4 4 3 2 86 88 2 6 6 6 72 57 9 8 5 5 75 83 5 10 3
3	3	4	4 4 3 3 255 255 4 7 1 206 212 3 8 6 0 82 87 4 10 3
3	3	4	4 4 3 4 462 459 7 7 1 52 53 4 8 6 1 18 75 4 10 4 0
3	3	4	4 4 3 4 57 65 3 7 2 1 198 178 3 8 6 2 62 75 4 10 4 0
3	3	4	4 4 3 5 253 258 4 7 2 2 81 71 3 8 6 3 32 18 7* 10 4
3	3	4	4 4 3 6 0 8 9* 7 3 0 213 202 4 8 6 4 82 82 3 10 4
3	3	4	4 4 4 104 112 3 7 3 1 26 31 6* 8 6 5 0 8 11* 10 4
3	3	4	4 4 4 239 232 4 7 3 2 174 158 3 8 6 6 55 47 8 10 4
3	3	4	4 4 4 5 1 0 25 22 6* 7 3 3 1 179 179 3 8 7 1 66 64 4 10 5
3	3	4	4 4 4 5 2 255 261 4 7 4 1 179 179 3 8 7 2 9 15 11* 10 5
3	3	4	4 4 4 5 5 2 25 22 6* 7 4 2 0 10 9* 8 7 3 74 69 4 10 5
3	3	4	4 4 4 5 5 3 0 292 326 5 7 7 4 3 141 154 3 8 7 4 0 7 12* 10 5
3	3	4	4 4 4 5 5 3 1 46 72 3 7 4 4 4 40 32 7 8 7 5 55 47 6 10 6
3	3	4	4 4 4 5 5 3 2 287 288 4 7 5 0 135 139 3 8 8 0 58 59 11 10 6
3	3	4	4 4 4 5 5 3 48 26 3 7 5 1 18 9 10* 8 8 1 0 7 15* 10 6 2
3	3	4	4 4 4 5 5 4 1 341 330 5 7 5 2 141 156 3 8 8 2 58 57 7 11 1
3	3	4	4 4 4 5 5 4 2 28 29 4 7 5 3 18 12 10* 8 8 3 0 5 14* 11 1
3	3	4	4 4 4 5 5 4 3 133 146 2 7 5 4 91 94 3 9 1 0 156 154 3 11 2
3	3	4	4 4 4 5 5 4 4 0 44 10* 7 5 5 0 0 12* 9 1 1 15 8 12* 11 2
3	3	4	4 4 4 5 5 5 0 334 321 5 7 6 1 102 114 3 9 2 1 116 117 3 11 3
3	3	4	4 4 4 5 5 5 1 0 0 10* 7 6 2 0 11 10* 9 2 2 12 14 12* 11 3 1
3	3	4	4 4 4 5 5 5 1 215 205 4 7 6 3 91 101 3 9 3 0 93 89 4 11 3 2
3	3	4	4 4 4 5 5 5 1 23 11 8* 7 6 4 23 14 8* 9 3 1 12 3 10* 11 3 3
3	3	4	4 4 4 5 5 5 1 140 130 3 7 6 5 7 9 75 3 9 3 2 111 110 3 11 4
3	3	4	4 4 4 5 5 5 1 0 4 14* 7 6 6 5 18 10 13* 9 3 3 15 16 12* 11 4
3	3	4	4 4 4 5 5 5 1 212 185 3 7 7 7 0 74 94 6 9 4 1 90 86 3 3
3	3	4	4 4 4 5 5 5 1 233 239 4 7 7 1 0 6 12* 9 4 2 0 5 11* 11 4
3	3	4	4 4 4 5 5 5 1 77 75 3 7 7 7 5 111 110 3 11 4 1 43 43 7 5 12*





Structure Determination of CdATC

A colorless, block crystal ($0.26 \times 0.24 \times 0.12$ mm) of $\text{Cd}(\text{ATC})\text{Cd}(\text{H}_2\text{O})_6\cdot 4\text{H}_2\text{O}$ was coated with a light hydrocarbon-based inert oil and mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K; the detector was placed at a distance of 4.916 cm from the crystal. A total of 2500 frames were collected with a scan width of 0.3° in ω and phi with an exposure time of 30 s/frame. The frames were integrated with the Siemens SAINT software package with a narrow frame algorithm. The integration of the data using primitive cubic unit cell yielded a total of 25227 reflections to a maximum 2θ value of 52.70° of which 1000 were independent and 986 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on xyz centroids of 5471 reflections above $10 \sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were corrected for absorption using an empirical method (SADABS) with transmission coefficients ranging from 0.647 to 0.862. The structure was solved and refined with the Siemens SHELXTL (version 5.10) software package, using the noncentrosymmetric space group $P(-4)3m$ with $Z = 4$ for the formula. There are three different Cd atoms which sit on the special positions respectively; Cd(1) with (-4)2m site symmetry, Cd(2) with (-4)3m one and Cd(3) with 3m one. The Cd(3) atom is disordered over two sites and their (Cd(3) and Cd(3')) s.o.f.s were refined. The adamantane tetracarboxylate (ATC) sits also on a special position with a site symmetry of 3m and therefore 1/6 ATC is unique. Carboxylate oxygen atoms are disordered over three sites. All non-hydrogen atoms except for the disordered carboxylate oxygen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Refinement was carried out using full matrix least-squares. The final refinement based on F^2 converged to $R1(\text{obs}) = 0.0590$ and $wR2 = 0.1604$ (all data). Additional details are presented in Table 1 and are given as Supporting information.

Sheldrick, G. M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.

Sheldrick, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen: Gottingen, Germany, 1996.

Saint Plus, v. 6.01, Bruker Analytical X-ray, Madison, WI, 1999.

Table 1. Crystal data and structure refinement for CdATC.

Empirical formula	C14 H32 O18 Cd2		
Formula weight	713.20		
Temperature	158(2) K		
Wavelength	0.71073 Å		
Crystal system	Cubic		
Space group	P(-4)3m		
Unit cell dimensions	$a = 13.4677(7)$ Å	$\alpha = 90^\circ$	
	$b = 13.4677(7)$ Å	$\beta = 90^\circ$	
	$c = 13.4677(7)$ Å	$\gamma = 90^\circ$	
Volume	2442.8(2) Å ³		
Z	4		
Density (calculated)	1.939 Mg/m ³		
Absorption coefficient	1.822 mm ⁻¹		
F(000)	1424		
Crystal size	0.26 x 0.24 x 0.12 mm ³		
Theta range for data collection	1.51 to 26.35°.		
Index ranges	-16≤h≤16, -16≤k≤16, -16≤l≤16		
Reflections collected	25227		
Independent reflections	1000 [R(int) = 0.0401]		
Completeness to theta = 26.35°	100.0 %		
Absorption correction	SADABS		
Max. and min. transmission	0.862 and 0.647		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	1000 / 15 / 84		
Goodness-of-fit on F ²	1.196		
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1600		
R indices (all data)	R1 = 0.0595, wR2 = 0.1604		
Absolute structure parameter	0.03(18)		
Largest diff. peak and hole	3.267 and -1.346 e.Å ⁻³		

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for CdATC. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cd(1)	0	5000	0	23(1)
Cd(2)	5000	5000	5000	20(1)
Cd(3)	2740(1)	2740(1)	2740(1)	18(1)
O(1W)	2155(7)	3869(5)	3869(5)	55(2)
O(2W)	1604(7)	3233(14)	1604(7)	100(6)
Cd(3')	2360(20)	2360(20)	2360(20)	246(18)
C(1)	1188(7)	6153(10)	1188(7)	41(3)
C(2)	1823(8)	6824(10)	1823(8)	38(3)
C(3)	3815(9)	6185(9)	3815(9)	38(4)
C(4)	3172(10)	6828(10)	3172(10)	33(4)
C(5)	2503(4)	6189(8)	2503(4)	30(2)
C(6)	2499(4)	7501(4)	1183(8)	32(3)
O(1)	1570(20)	5602(15)	568(16)	63(6)
O(2)	287(15)	6160(20)	1270(20)	73(8)
O(1')	599(11)	6500(20)	599(11)	51(7)
O(2')	1220(20)	5233(17)	1220(20)	90(12)
O(3)	4410(10)	5590(10)	3417(19)	41(6)
O(4)	3740(18)	6260(18)	4723(16)	68(9)
O(3W)	3529(13)	271(10)	4666(9)	60(4)
O(4W)	1640(50)	0	0	250(30)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for CdATC.

Cd(1)-O(1')	2.32(3)	Cd(1)-O(1)	2.32(3)
Cd(1)-O(2')	2.35(4)	Cd(1)-O(2)	2.36(3)
Cd(2)-O(3)	2.41(3)	Cd(2)-O(4)	2.43(3)
Cd(3)-O(2W)	2.263(15)	Cd(3)-O(1W)	2.291(9)
O(2W)-Cd(3')	1.86(2)	C(1)-O(1')	1.21(2)
C(1)-O(2)	1.22(2)	C(1)-O(1)	1.23(2)
C(1)-O(2')	1.24(2)	C(1)-C(2)	1.51(2)
C(2)-C(6)	1.550(10)	C(2)-C(5)	1.552(14)
C(3)-O(4)	1.23(2)	C(3)-O(3)	1.25(2)
C(3)-C(4)	1.50(3)	C(4)-C(5)	1.538(12)
O(1')-Cd(1)-O(2')	52.8(9)	O(1)-Cd(1)-O(2)	52.8(9)
O(4)-Cd(2)-O(3)	53.4(9)	O(2W)-Cd(3)-O(2W)#1	86.6(7)
O(2W)-Cd(3)-O(2W)#2	86.6(7)	O(2W)#1-Cd(3)-O(2W)#2	86.6(7)
O(2W)-Cd(3)-O(1W)	91.2(3)	O(2W)#1-Cd(3)-O(1W)	177.0(5)
O(2W)#2-Cd(3)-O(1W)#1	177.0(5)	O(1W)-Cd(3)-O(1W)#1	90.9(4)
O(2W)-Cd(3)-O(1W)#2	177.0(5)	O(2W)#1-Cd(3)-O(1W)#2	91.2(3)
O(2W)#1-Cd(3)-O(1W)#2	91.2(3)	O(1W)-Cd(3)-O(1W)#2	90.9(4)
O(1W)#1-Cd(3)-O(1W)#2	90.9(4)	O(2W)-Cd(3)-O(2W)#1	113.2(13)
O(2W)-Cd(3)-O(2W)#2	113.2(13)	O(2W)#1-Cd(3)-O(2W)#2	113.2(13)
O(2)-C(1)-O(1)	119(2)	O(1')-C(1)-O(2')	115(3)
O(1')-C(1)-C(2)	120.8(17)	O(2)-C(1)-C(2)	120.2(17)
O(1)-C(1)-C(2)	120.7(15)	O(2')-C(1)-C(2)	124(2)
C(1)-C(2)-C(6)#3	111.7(8)	C(1)-C(2)-C(6)	111.7(8)
C(6)#3-C(2)-C(6)	107.8(10)	C(1)-C(2)-C(5)	109.8(10)
C(6)#3-C(2)-C(5)	107.8(8)	C(6)-C(2)-C(5)	107.8(8)
O(4)-C(3)-O(3)	122(3)	O(4)-C(3)-C(4)	118.7(19)
O(3)-C(3)-C(4)	119.4(14)	C(3)-C(4)-C(5)	110.7(9)
C(3)-C(4)-C(5)#4	110.7(9)	C(5)-C(4)-C(5)#4	108.3(9)
C(3)-C(4)-C(5)#3	110.7(9)	C(5)-C(4)-C(5)#3	108.2(9)
C(5)#4-C(4)-C(5)#3	108.3(9)	C(4)-C(5)-C(2)	112.5(14)
C(2)#4-C(6)-C(2)	112.5(15)	C(1)-O(2)-Cd(1)	94.9(17)
C(1)-O(1')-Cd(1)	97.1(17)	C(1)-O(2')-Cd(1)	95(2)
C(3)-O(3)-Cd(2)	92.4(16)	C(3)-O(4)-Cd(2)	92(2)

Symmetry transformations used to generate equivalent atoms:

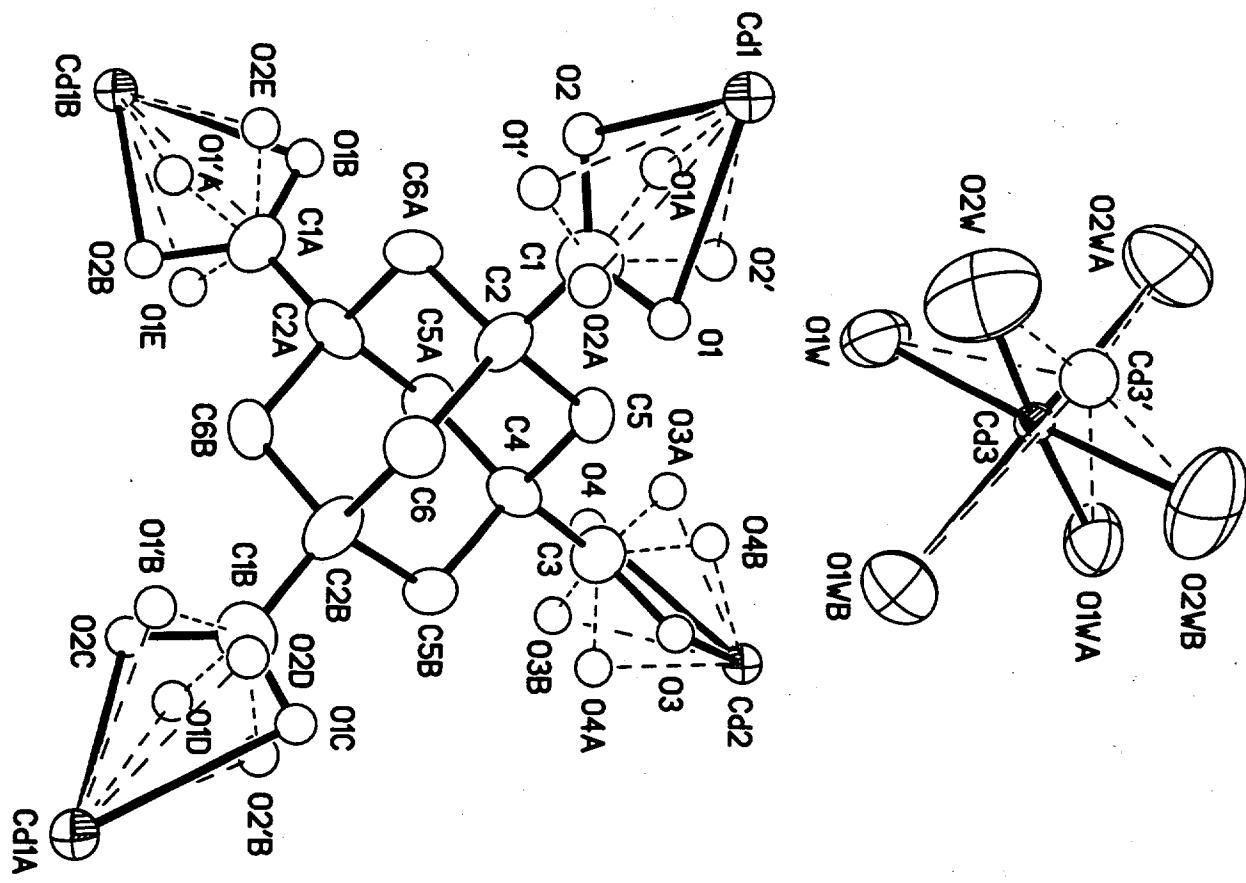
#1 y,z,x #2 z,x,y #3 z,-x+1,-y+1 #4 -y+1,-z+1,x

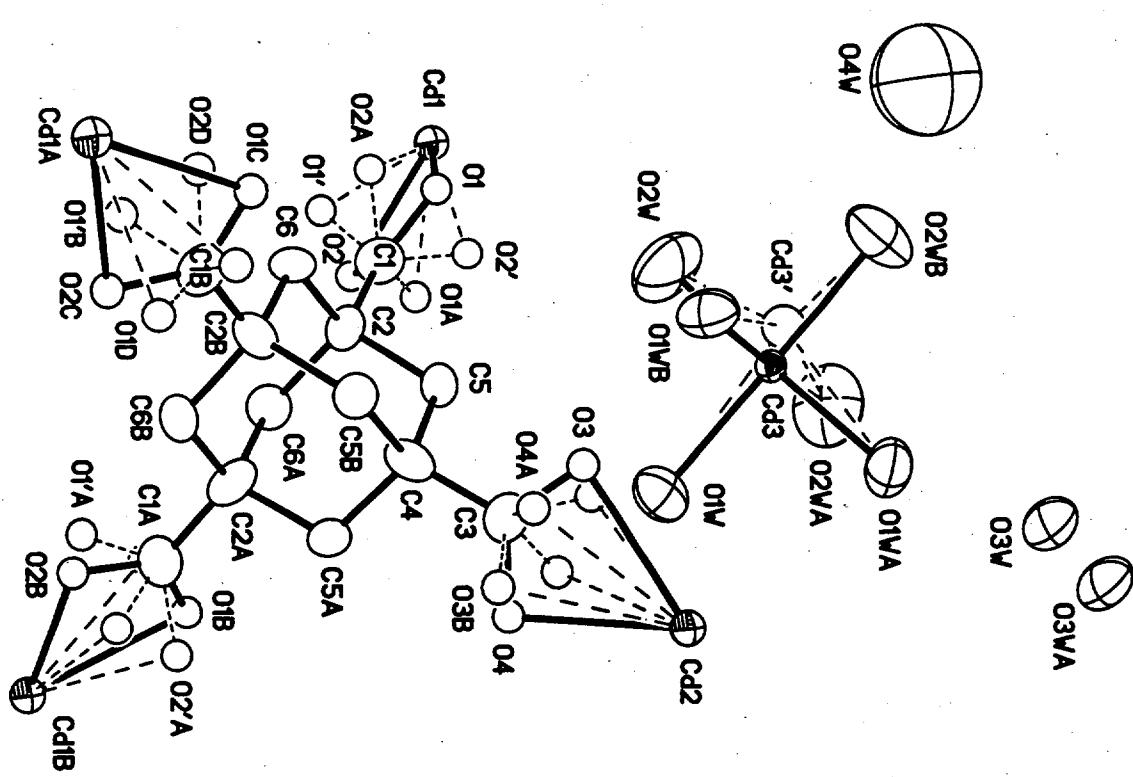
Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for CdATC. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cd(1)	23(1)	23(1)	23(1)	0	0	0
Cd(2)	20(1)	20(1)	20(1)	0	0	0
Cd(3)	18(1)	18(1)	18(1)	1(1)	1(1)	1(1)
O(1W)	40(5)	63(3)	63(3)	-11(4)	5(3)	5(3)
O(2W)	83(7)	136(13)	83(7)	28(6)	-27(8)	28(6)
Cd(3')	246(18)	246(18)	246(18)	10(20)	10(20)	10(20)
C(1)	39(4)	46(7)	39(4)	-2(4)	-9(5)	-2(4)
C(2)	39(4)	36(6)	39(4)	13(5)	15(6)	13(5)
C(3)	38(4)	38(4)	38(4)	4(5)	-4(5)	4(5)
C(4)	33(4)	33(4)	33(4)	-10(5)	10(5)	-10(5)
C(5)	34(4)	22(5)	34(4)	1(2)	-1(4)	1(2)
C(6)	38(4)	38(4)	21(5)	-2(2)	2(2)	1(4)
O(3W)	72(11)	59(9)	47(7)	16(6)	5(7)	4(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for CdATC.

	x	y	z	U(eq)
H(5A)	2910	5777	2094	36
H(6A)	2919	7081	750	39
H(6B)	2079	7921	751	39





X-ray crystallography of ZnATB

A colorless, needle crystal ($0.30 \times 0.06 \times 0.04$ mm) of $\text{Zn}_2(\text{ATB})(\text{H}_2\text{O})\cdot(7\text{H}_2\text{O})$ was coated with a light hydrocarbon-based inert oil and mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 223(2) K; the detector was placed at a distance of 5.028 cm from the crystal. The collected frames were integrated with the Siemens SAINT software package with a narrow frame algorithm. The integration of the data using triclinic unit cell yielded a total of 14526 reflections to a maximum 2θ value of 37.68° of which 1512 were independent and 689 were greater than $2\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were corrected for absorption using an empirical method (SADABS) with transmission coefficients ranging from 0.871 to 1.000. The structure was solved by direct methods and the subsequent difference Fourier methods and refined with the Siemens SHELXTL (version 5.10) software package, using the centrosymmetric space group *Imma* (No. 74) with $Z = 4$ for the formula. All nonhydrogen atoms of the framework except for the disordered carboxylate oxygen atoms (O3 and O3') were refined anisotropically with the aromatic hydrogen atoms generated and fixed in idealized positions. Disordered water molecules with half occupancies were refined isotropically. Final full matrix least-squares refinement on F^2 converged to $R1 = 0.1064$ ($I > 2\sigma(I)$) and $wR2 = 0.3210$ (all data) with GOF = 0.999. Additional details are presented in Table 1 and are given as Supporting Information.

Sheldrick, G. M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.

Sheldrick, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen: Gottingen, Germany, 1996.

Saint Plus, v. 6.01, Bruker Analytical X-ray, Madison, WI, 1999.

Table 1. Crystal data and structure refinement for ZnATB.

Identification code	ZnATB
Empirical formula	C38 H44 O16 Zn2
Formula weight	887.47
Temperature	223(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Imma (No. 74)
Unit cell dimensions	a = 19.561(6) Å b = 15.255(5) Å c = 23.404(7) Å
	α = 90°. β = 90°. γ = 90°.
Volume	6984(4) Å ³
Z	4
Density (calculated)	0.844 Mg/m ³
Absorption coefficient	0.728 mm ⁻¹
F(000)	1840
Crystal size	0.30 x 0.06 x 0.04 mm ³
Theta range for data collection	1.59 to 18.84°.
Index ranges	-17<=h<=17, -13<=k<=13, -21<=l<=21
Reflections collected	14526
Independent reflections	1512 [R(int) = 0.2148]
Completeness to theta = 18.84°	99.9 %
Absorption correction	SADABS
Max. and min. transmission	1.000 and 0.871
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1512 / 17 / 145
Goodness-of-fit on F ²	0.999
Final R indices [I>2sigma(I)]	R1 = 0.1064, wR2 = 0.2895
R indices (all data)	R1 = 0.1766, wR2 = 0.3210
Extinction coefficient	0.0018(5)
Largest diff. peak and hole	0.632 and -0.439 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ZnATB. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zn(1)	765(1)	2500	7162(1)	83(2)
O(1)	561(6)	3507(7)	7677(5)	85(4)
O(2)	0	2500	6650(9)	157(13)
C(1)	653(11)	7500	10225(9)	63(6)
C(2)	633(7)	6677(10)	9861(6)	67(5)
C(3)	0	6694(16)	9479(9)	57(6)
C(4)	0	7500	9092(11)	44(8)
C(5)	0	7500	10592(11)	61(9)
C(6)	1292(12)	7500	10608(10)	81(8)
C(7)	1895(11)	7500	10331(11)	195(19)
C(8)	2493(12)	7500	10616(11)	165(10)
C(9)	2526(15)	7500	11190(10)	165(10)
C(10)	1942(13)	7500	11490(11)	111(11)
C(11)	1364(12)	7500	11179(10)	98(10)
C(12)	3270(20)	7500	11441(9)	183(19)
C(13)	0	5914(18)	9088(10)	63(7)
C(14)	571(9)	5540(15)	8871(10)	127(8)
C(15)	572(9)	4867(15)	8474(10)	120(8)
C(16)	0	4498(17)	8259(10)	59(6)
C(17)	0	3783(17)	7830(11)	60(6)
O(1W)	2500	9640(30)	12500	450(30)
O(2W)	2110(30)	7500	8680(20)	410(30)
O(3W)	2600(40)	5000	10000	330(40)
O(4W)	0	330(50)	6390(30)	320(40)
O(5W)	1640(60)	7500	7600(50)	520(70)
O(3)	3276(8)	7804(12)	11933(7)	110(7)
O(3')	3611(17)	8190(20)	11397(15)	91(13)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for ZnATB.

Zn(1)-O(2)	1.917(13)	Zn(1)-O(1)	1.994(12)
Zn(1)-O(3)#2	2.005(15)	Zn(1)-O(3')#2	2.41(4)
Zn(1)-C(12)#3	2.53(4)	Zn(1)-Zn(1)#4	2.992(6)
O(1)-C(17)	1.228(13)	O(2)-Zn(1)#4	1.917(13)
C(1)-C(2)#5	1.517(17)	C(1)-C(2)	1.517(17)
C(1)-C(5)	1.54(2)	C(1)-C(6)	1.54(3)
C(2)-C(3)	1.526(17)	C(3)-C(13)	1.50(3)
C(3)-C(2)#6	1.526(17)	C(3)-C(4)	1.53(2)
C(4)-C(3)#7	1.53(2)	C(5)-C(1)#7	1.54(2)
C(6)-C(11)	1.343(11)	C(6)-C(7)	1.345(11)
C(7)-C(8)	1.348(11)	C(8)-C(9)	1.345(11)
C(9)-C(10)	1.339(11)	C(9)-C(12)	1.57(5)
C(10)-C(11)	1.344(11)	C(12)-O(3)	1.241(10)
C(12)-O(3)#5	1.241(10)	C(12)-O(3')	1.254(10)
C(12)-O(3')#5	1.254(10)	C(12)-Zn(1)#8	2.53(4)
C(13)-C(14)	1.35(2)	C(13)-C(14)#6	1.35(2)
C(14)-C(15)	1.38(3)	C(15)-C(16)	1.35(2)
C(16)-C(15)#6	1.35(2)	C(16)-C(17)	1.48(3)
C(17)-O(1)#6	1.228(13)	O(3)-Zn(1)#8	2.005(15)
O(3')-Zn(1)#8	2.41(4)		
O(2)-Zn(1)-O(1)#1	102.8(4)	O(2)-Zn(1)-O(1)	102.8(4)
O(1)#1-Zn(1)-O(1)	100.8(6)	O(2)-Zn(1)-O(3)#2	124.3(7)
O(1)#1-Zn(1)-O(3)#2	121.8(6)	O(1)-Zn(1)-O(3)#2	99.8(6)
O(2)-Zn(1)-O(3)#3	124.3(7)	O(1)#1-Zn(1)-O(3')#3	99.8(6)
O(1)-Zn(1)-O(3)#3	121.8(6)	O(3)#2-Zn(1)-O(3')#3	26.7(10)
O(2)-Zn(1)-O(3')#2	86.0(9)	O(1)#1-Zn(1)-O(3')#2	152.7(7)
O(1)-Zn(1)-O(3')#2	102.3(9)	O(3)#2-Zn(1)-O(3')#2	39.4(8)
O(3)#3-Zn(1)-O(3')#2	55.2(8)	O(2)-Zn(1)-O(3')#3	86.0(9)
O(1)#1-Zn(1)-O(3')#3	102.3(9)	O(1)-Zn(1)-O(3')#3	152.7(7)
O(3)#2-Zn(1)-O(3')#3	55.2(8)	O(3)#3-Zn(1)-O(3')#3	39.4(8)
O(3')#2-Zn(1)-O(3')#3	52.0(15)	O(2)-Zn(1)-C(12)#3	99.5(10)
O(1)#1-Zn(1)-C(12)#3	123.5(4)	O(1)-Zn(1)-C(12)#3	123.5(4)
O(3')#2-Zn(1)-C(12)#3	28.9(7)	O(3)#3-Zn(1)-C(12)#3	28.9(7)

O(3')#2-Zn(1)-C(12)#3	29.3(4)	O(3')#3-Zn(1)-C(12)#3	29.3(4)
O(2)-Zn(1)-Zn(1)#4	38.7(5)	O(1)#1-Zn(1)-Zn(1)#4	78.4(3)
O(1)-Zn(1)-Zn(1)#4	78.4(3)	O(3')#2-Zn(1)-Zn(1)#4	159.3(5)
O(3)#3-Zn(1)-Zn(1)#4	159.3(5)	O(3')#2-Zn(1)-Zn(1)#4	120.4(7)
O(3')#3-Zn(1)-Zn(1)#4	120.4(7)	C(12)#3-Zn(1)-Zn(1)#4	138.2(9)
C(17)-O(1)-Zn(1)	128.3(16)	Zn(1)#4-O(2)-Zn(1)	102.6(10)
C(2)#5-C(1)-C(2)	111.6(17)	C(2)#5-C(1)-C(5)	107.0(12)
C(2)-C(1)-C(5)	107.0(12)	C(2)#5-C(1)-C(6)	110.4(11)
C(2)-C(1)-C(6)	110.4(11)	C(5)-C(1)-C(6)	110.4(16)
C(1)-C(2)-C(3)	109.6(16)	C(13)-C(3)-C(2)	110.1(13)
C(13)-C(3)-C(2)#6	110.1(13)	C(2)-C(3)-C(2)#6	108.4(17)
C(13)-C(3)-C(4)	106.0(16)	C(2)-C(3)-C(4)	111.1(14)
C(2)#6-C(3)-C(4)	111.1(14)	C(3)#7-C(4)-C(3)	107(2)
C(1)#7-C(5)-C(1)	112(2)	C(11)-C(6)-C(7)	113(2)
C(11)-C(6)-C(1)	132(2)	C(7)-C(6)-C(1)	115.6(19)
C(6)-C(7)-C(8)	122(2)	C(9)-C(8)-C(7)	122(3)
C(10)-C(9)-C(8)	119(3)	C(10)-C(9)-C(12)	127(2)
C(8)-C(9)-C(12)	115(2)	C(9)-C(10)-C(11)	116(2)
C(6)-C(11)-C(10)	129(2)	O(3)-C(12)-O(3)#5	43.8(18)
O(3)-C(12)-O(3')	76(2)	O(3)#5-C(12)-O(3')	113(3)
O(3)-C(12)-O(3')#5	113(3)	O(3)#5-C(12)-O(3')#5	76(2)
O(3')-C(12)-O(3')#5	115(6)	O(3)-C(12)-C(9)	111(3)
O(3')#5-C(12)-C(9)	111(3)	O(3')-C(12)-C(9)	117(3)
O(3')#5-C(12)-C(9)	117(3)	O(3)-C(12)-Zn(1)#8	51.4(17)
O(3')#5-C(12)-Zn(1)#8	51.4(17)	O(3')-C(12)-Zn(1)#8	70(3)
O(3')#5-C(12)-Zn(1)#8	70(3)	C(9)-C(12)-Zn(1)#8	160(2)
C(14)-C(13)-C(14)#6	111(2)	C(14)-C(13)-C(3)	124.2(13)
C(14)#6-C(13)-C(3)	124.2(13)	C(13)-C(14)-C(15)	124.3(18)
C(16)-C(15)-C(14)	124.0(19)	C(15)-C(16)-C(15)#6	112(2)
C(15)-C(16)-C(17)	124.0(12)	C(15)#6-C(16)-C(17)	124.0(12)
O(1)#6-C(17)-O(1)	127(3)	O(1)#6-C(17)-C(16)	116.7(14)
O(1)-C(17)-C(16)	116.7(14)	O(3)#5-O(3)-C(12)	68.1(9)
O(3)#5-O(3)-Zn(1)#8	76.6(5)	C(12)-O(3)-Zn(1)#8	100(2)
C(12)-O(3')-O(3)	51.6(11)	C(12)-O(3')-Zn(1)#8	81(3)

Symmetry transformations used to generate equivalent atoms:

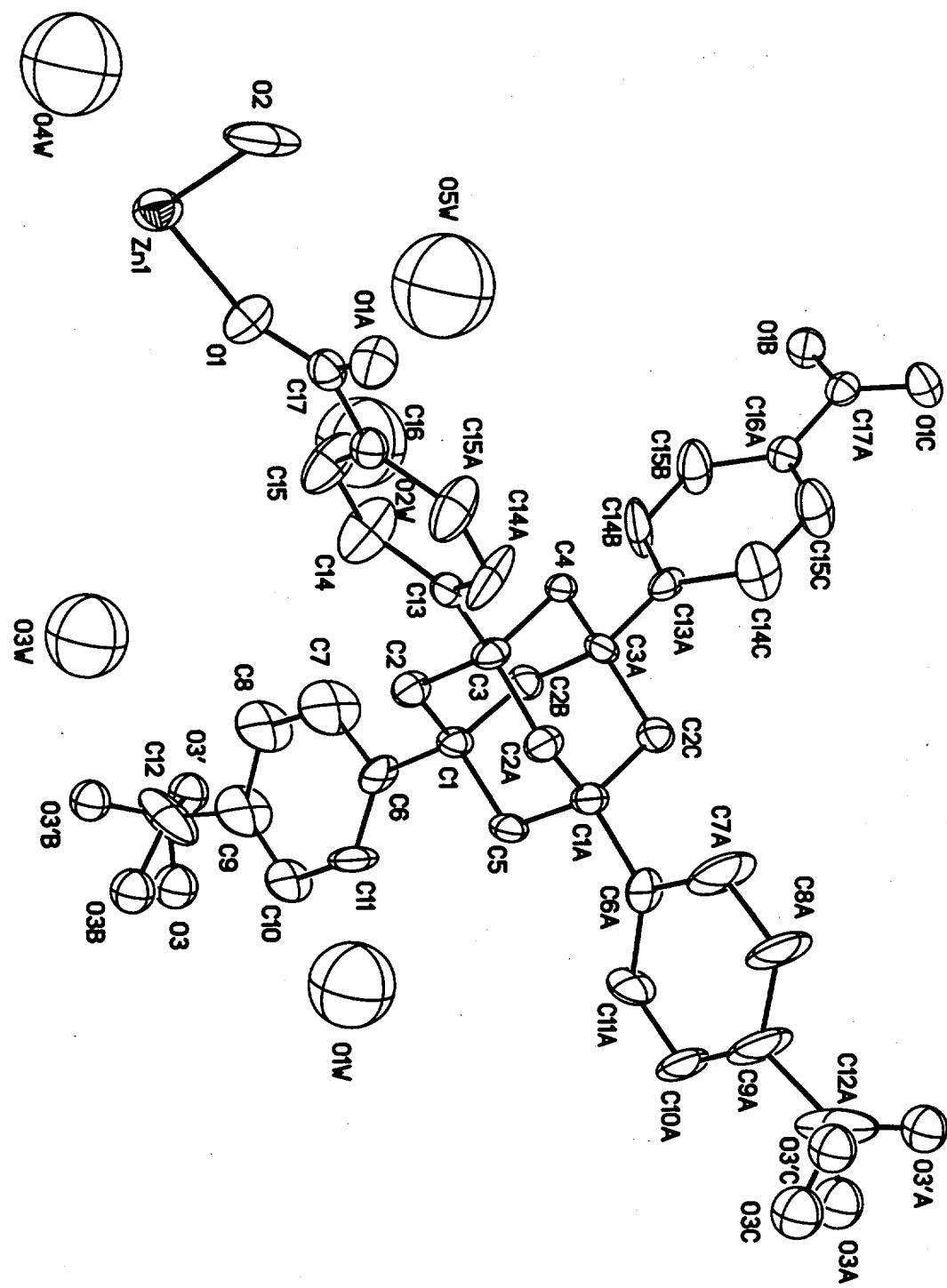
```
#1 x,-y+1/2,z  #2 -x+1/2,y-1/2,z-1/2  #3 -x+1/2,-y+1,z-1/2  
#4 -x,-y+1/2,z  #5 x,-y+3/2,z  #6 -x,y,z  #7 -x,-y+3/2,z  
#8 -x+1/2,-y+1,z+1/2
```

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ZnATB. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* a^2 U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	76(2)	105(3)	68(2)	0	12(2)	0
O(1)	78(10)	81(8)	95(9)	-26(7)	15(7)	-1(8)
O(2)	84(17)	360(40)	33(14)	0	0	0
C(1)	50(17)	90(20)	45(14)	0	-3(14)	0
C(2)	56(11)	84(13)	59(11)	-10(10)	-3(9)	-1(10)
C(3)	54(17)	79(19)	39(14)	-18(16)	0	0
C(4)	35(18)	70(20)	33(18)	0	0	0
C(5)	70(20)	80(30)	33(19)	0	0	0
C(6)	25(16)	130(30)	90(20)	0	15(16)	0
C(7)	70(20)	390(60)	120(30)	0	-60(20)	0
C(8)	85(15)	310(30)	101(18)	0	-70(20)	0
C(9)	85(15)	310(30)	101(18)	0	-70(20)	0
C(10)	64(19)	200(30)	70(20)	0	-38(19)	0
C(11)	90(20)	160(30)	37(18)	0	22(17)	0
C(12)	350(60)	110(30)	90(30)	0	-100(30)	0
C(13)	31(16)	110(20)	52(16)	22(18)	0	0
C(14)	55(15)	141(19)	190(20)	-87(18)	-13(14)	-30(14)
C(15)	59(15)	126(18)	170(20)	-73(18)	14(14)	-10(14)
C(16)	60(20)	50(18)	64(17)	3(16)	0	0
C(17)	60(20)	60(20)	61(18)	11(18)	0	0

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ZnATB.

	x	y	z	U(eq)
H(2A)	634	6145	10105	80
H(2B)	1054	6619	9630	80
H(4)	-399	7500	8838	53
H(5)	0	8011	10865	74
H(7)	1933	7500	9910	234
H(8)	2932	7500	10436	198
H(10)	1888	7500	11922	133
H(11)	914	7500	11374	118
H(14)	1015	5750	9012	153
H(15)	1025	4647	8341	144



Introduction

The cation and anion crystallize in the orthorombic space group $P2_12_12_1$ with four molecules in the unit cell. The asymmetric unit also includes 8 water molecules, four of which are attached to Ni centers. Of the water molecules not directly bonded to Ni, one is ordered and three are disordered. The disorder was modeled by linking the occupancies of atomic positions near each other so that the sum of the nearest neighbors was unity and the sum of any neighbors within van der Waals contact did not exceed unity. The positional and thermal parameters of the oxygen atoms thus refined converged to reasonable values, lending credence to the model.

The two nickel centers are joined together in a dimer ($\text{Ni1...Ni2} = 3.43\text{\AA}$) with two bridging carboxylates and a bridging water molecule. Each nickel atom is roughly octahedrally coordinated. The coordination of Ni1 is completed by three water molecules. The coordination of Ni2 is completed by a chelating carboxylate from a neighboring ligand and by monodentate coordination by O8 from yet another ligand. There is a clear hydrogen bond between the bridging water, O9, and the other oxygen of the last carboxylate. The coordination of the dimer by the bridging carboxylates is somewhat irregular; the Ni...Ni vector is significantly skew to both of the O...O vectors of the bridging carboxylate ligands. The whole ionic array forms a three-dimensional infinite lattice as each of the four tetrahedrally arrayed carboxylates bonds to a different symmetry-related Ni dimer. The remaining water molecules pack into the interstices of this array and form presumed hydrogen bonds to each other and to the oxygens coordinated to the Ni.

The bonding distances to the Ni are variable. The longest distances are to the chelating carboxylate group, intermediate for coordinated water and shortest for the bridging carboxyl ligands and the monodentate carboxylate. The range is from 1.98\AA to 2.12\AA ; all are tightly bonded.

Distances within the adamantly carboxylate are quite regular and unexceptional.

Experimental

Data Collection

A pale green needlelike crystal of $\text{Ni}_2\text{O}_{16}\text{C}_{14}\text{H}_{28}$ having approximate dimensions of $0.15 \times 0.15 \times 0.05$ mm was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on a SMART¹⁰ CCD area detector with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 4726 reflections in the range $3.00 < 2\theta < 45.00^\circ$ corresponded to a primitive orthorhombic cell with dimensions:

$$\begin{aligned}a &= 10.0656(3) \text{\AA} \\b &= 11.1625(3) \text{\AA} \\c &= 19.2011(2) \text{\AA} \\V &= 2157.38(9) \text{\AA}^3\end{aligned}$$

For Z = 4 and F.W. = 569.77, the calculated density is 1.75 g/cm³. The systematic absences of:

$$h00: h \neq 2n$$

$$0k0: k \neq 2n$$

00l: $l \neq 2n$

uniquely determine the space group to be:

P2₁2₁2₁ (#19)

The data were collected at a temperature of -114 \pm 1°C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10.0 seconds per frame.

Data Reduction

Data were integrated by the program SAINT¹¹ to a maximum 2θ value of 51.1°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP¹². An empirical absorption correction based on comparison of redundant and equivalent reflections as applied using XPREP (Tmax = 0.89, Tmin = 0.82).

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement³ was based on 2941 observed reflections ($I > 3.00\sigma(I)$) and 233 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.029$$

$$R_w = \sqrt{(\Sigma w(|Fo| - |Fc|)^2) / \Sigma wFo^2} = 0.037$$

The standard deviation of an observation of unit weight⁴ was 1.37. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin \theta / \lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.48 and -0.37 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in Fcalc⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbel⁸. All calculations were performed using the teXsan⁹ crystallographic software package of Molecular Structure Corporation.

References

(1) SIR92: Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A. (1993). *J. Appl. Cryst.*, 26, 343.

(2) DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel,

R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(3) Least-Squares:

$$\text{Function minimized: } \Sigma w(|F_o| - |F_c|)^2$$

(4) Standard deviation of an observation of unit weight:

$$\sqrt{\Sigma w(|F_o| - |F_c|)^2 / (N_o - N_v)}$$

where: No = number of observations

Nv = number of variables

(5) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(6) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(7) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(8) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(9) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).

(10) SMART: Area-Detector Software Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (1995-99)

(11) SAINT: SAX Area-Dectector Integration Program, V5.04; Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(12) XPREP:(v 5.03) Part of the SHELXTL Crystal Structure Determination Siemens Industrial Automation, Inc.: Madison, WI, (1995)

(13) SADABS: Siemens Area Detector ABSorption correction program, George Sheldrick, (1996). Advance copy, private communication.

EXPERIMENTAL DETAILS**A. Crystal Data**

Empirical Formula	Ni ₂ O ₁₆ C ₁₄ H ₂₈
Formula Weight	569.77
Crystal Color, Habit	pale, needlelike
Crystal Dimensions	0.15 X 0.15 X 0.05 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	$a = 10.0656(3) \text{ \AA}$ $b = 11.1625(3) \text{ \AA}$ $c = 19.2011(2) \text{ \AA}$ $V = 2157.38(9) \text{ \AA}^3$
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)
Z value	4
D _{calc}	1.754 g/cm ³
F ₀₀₀	1184.00
$\mu(\text{MoK}\alpha)$	40.13 cm ⁻¹

B. Intensity Measurements

Diffractometer	SMART CCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
2 θ_{max}	51.1°

No. of Reflections Measured Total: 9647
 Unique: 2357 ($R_{int} = 0.038$)

Corrections Lorentz-polarization
 Absorption ($T_{max} = 0.89$, $T_{min} = 0.82$)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(Fo - Fc)^2$
Least Squares Weights	$w = \frac{1}{\sigma^2(Fo)} = [\sigma_c^2(Fo) + \frac{p^2}{4} Fo^2]^{-1}$
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	2941
No. Variables	233
Reflection/Parameter Ratio	12.62
Residuals: R; R_w ; R_{all}	0.029 ; 0.037; 0.038
Goodness of Fit Indicator	1.37
Max Shift/Error in Final Cycle	0.01
Maximum peak in Final Diff. Map	$0.48 e^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.37 e^-/\text{\AA}^3$