

Supporting Information

**A 30-Membered Nonanuclear Cobalt(II) Macrocycle Containing
Phosphonate-bridged Trinuclear Sub-units**

Dipankar Sahoo,^a Ramakirushnan Suriyanarayanan^a and Vadapalli Chandrasekhar*^a,

^a Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur - 208016, India.

^b National Institute of Science Education and Research, Institute of Physics Campus, Sachivalaya Marg, Sainik School Road, Bhubaneswar-751005, Orissa, India

Experimental

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.^{S1} The following chemicals were used as obtained: $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, U.S.A.), triethylamine (S.D. fine Chemicals, India), AlCl_3 (S.D. Fine Chemicals, India), PCl_3 (S.D. Fine Chemicals, India), 2,4-pentanedione (S.D. Fine Chemicals, India), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$; S.D. Fine Chemicals, India) and acetonitrile (S.D. Fine Chemicals, India). 3,5-Dimethyl-1*H*-pyrazole^{S2} and (trichloromethyl)phosphonic acid ($\text{Cl}_3\text{CPO}_3\text{H}_2$)^{S3} were prepared according to literature procedures.

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer Spectrum Version FT IR spectrophotometer operating at $400\text{-}4000\text{ cm}^{-1}$. Elemental analyses of the compounds were obtained on a Thermoquest CE instruments CHNS-O, EA/110 model. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer.

Synthesis of 1. $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.112 g, 0.305 mmol) was taken in acetonitrile (25 mL). To this a solution of 3,5-dimethyl-1*H*pyrazole (0.0586 g, 0.610 mmol) and (trichloromethyl)phosphonic acid (0.0203 g, 0.102 mmol) in acetonitrile (15 mL) was added, and the resulting mixture was stirred at room temperature for 24 h. At this stage, triethylamine (0.083 g, 0.814 mmol) was added to the reaction mixture. The resulting clear colorless solution was stirred for an additional 24 h. The solution was evaporated, and the residue obtained was re-dissolved in toluene and kept for crystallization by vapor diffusion method with *n*-hexane. After 8-9 days, violet block-shaped crystals of **1** was obtained. Yield: 0.038 g, ~ 32% (based on cobalt) mp: >200 °C. Anal. Calcd. for $\text{C}_{142}\text{H}_{189}\text{Cl}_9\text{Co}_9\text{N}_{18}\text{O}_9\text{P}_3$ (**1**; 3486.64): C, 52.73; H, 5.89; N, 7.79;

Found: C, 52.64; H, 5.81; N, 7.70. IR (KBr, ν/cm^{-1}): 2924 (w, br), 2855 (w), 1527 (s), 1416 (s) 1335 (m), 1318 (m), 1149 (s), 1042 (s), 1026 (s), 757 (m), 627 (w), 551(m), 426 (w). ESI-MS (m/z): 963.56 $[\text{Co}_3(3,5\text{-DMPz})_4(3,5\text{-DMPzH})_2(\text{Cl}_3\text{CPO}_3) + \text{H}_2\text{O} + \text{H}^+]^+$ (Supporting Information).

X-ray Crystallography.

Data were collected on Bruker APEX II CCD diffractometer (MoK_α , $\lambda = 0.71073 \text{ \AA}$). Complete hemispheres of data were collected using ω -scans (0.3° , up to 30 s/frame). Integrated intensities were obtained with SAINT+,^{S4} and when they were corrected for absorption SADABS was used.^{S5} Structure solution and refinement was performed with the SHELXTL-package.^{S6} The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against F^2 .^{S7} All the other non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms on the carbon frameworks were included in the final stages of the refinement and were refined with a typical riding model. Some solvent molecules could not be modeled satisfactorily as they were located on the symmetry elements of the space group. Therefore the Olex/Mask^{S8} was used to remove such disordered units from the respective overall intensity data. The details of the masked electron density are appended to the respective cif files. The sample diffracted very weakly, and at high angles the reflections were absent. Despite the poor quality of the data, the connectivity and gross conformation are not in doubt. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].

Mask Details for 1.

Electron count 128.4 (void of 227.4 Å³) per unit cell accounts for one toluene molecule. [128.4 total no. of calculated e⁻ (Z = 2)]

References:

- (S1) (a) B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Text Book of Practical Organic Chemistry*, 5th edn, ELBS and Longman, London, UK, **1989**. (b) Williams D. B. G.; Lawton, M. *J. Org. Chem.* **2010**, *75*, 8351.
- (S2) (a) Wiley R. H.; Hexner, P. E. *Org. Synth.* **1951**, *31*, 43. (b) Wiley, R. H.; Hexner, P. E. *Org. Synth.* **1963**, *4*, 351.
- (S3) Bengelsdorf, S.; Barron, L. B. *J. Am. Chem. Soc.* **1955**, *77*, 2869.
- (S4) *SMART & SAINT Software Reference Manuals, version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003*.
- (S5) G. M. Sheldrick, *SADABS a Software for Empirical Absorption Correction, version 2.05*; University of Göttingen: Göttingen, Germany, **2002**.
- (S6) G. M. Sheldrick, *SHELXTL, version 6.12; Bruker AXS Inc. Madison, WI, 2001*.
- (S7) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, **1997**.
- (S8) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339.

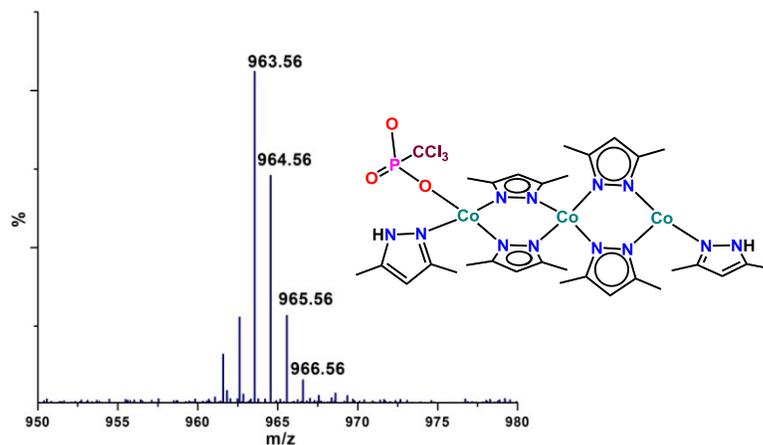


Figure S1. ESI-MS of **1** showing the molecule is fragmented under the condition employed for data collection.

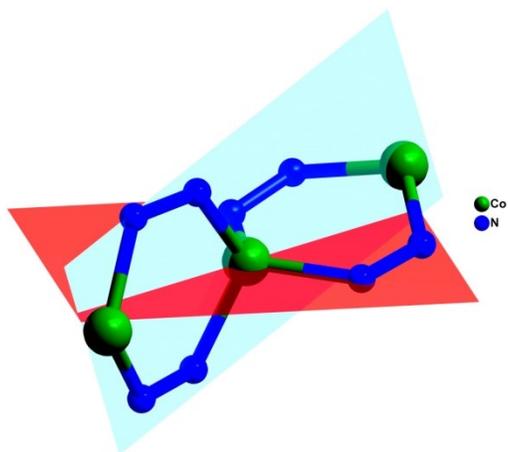


Figure S2. Intersection of the two planes formed by the two adjacent Co₂N₂ rings.

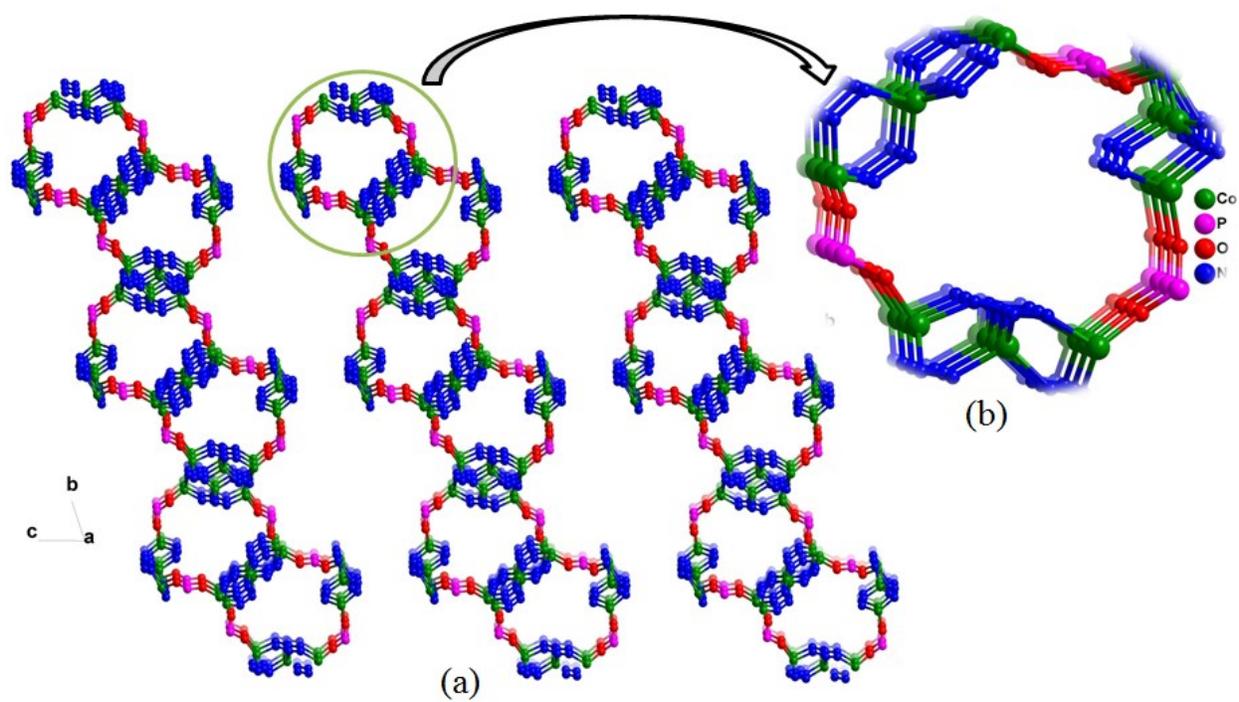


Figure S3. (a) Supramolecular architecture of **1** along the *a*-axis. (b) Supramolecular channel in **1**.

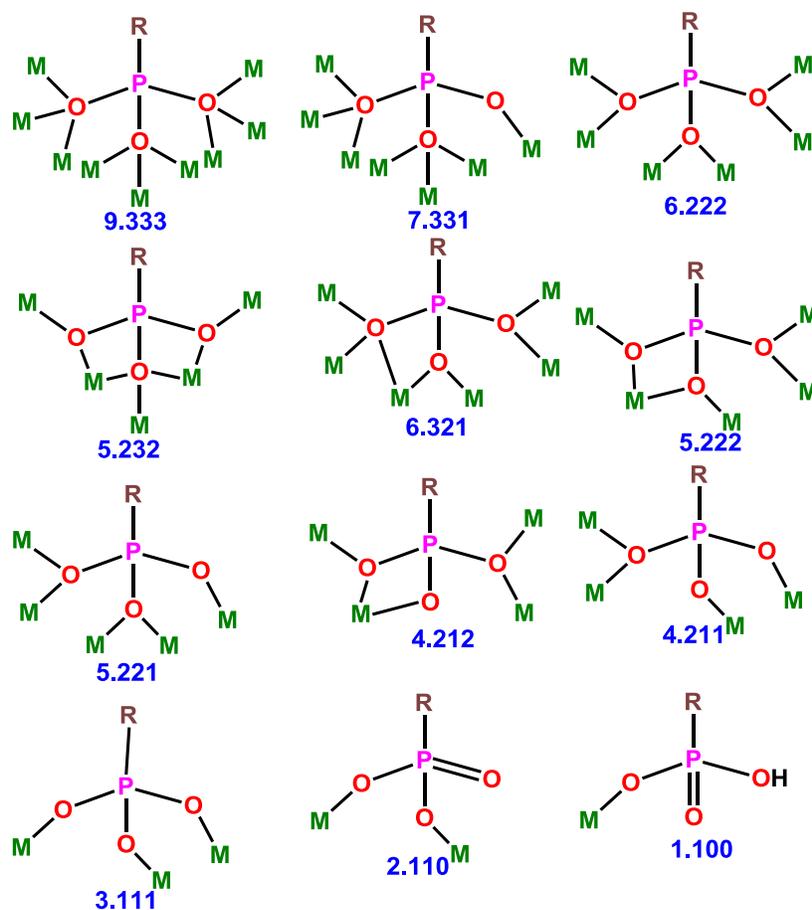


Chart S1. Binding capacity of phosphonate (Harris notation has been used).

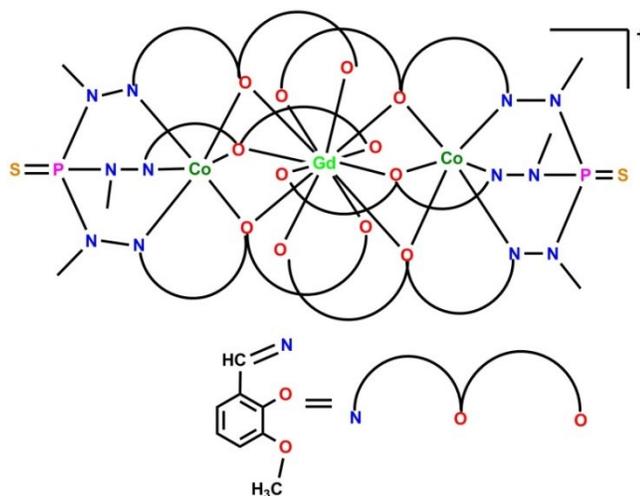


Chart S2. Schematic representation of $[\{(S)P[N(Me)N=CH-C_6H_3-2-O-3-OMe]_3\}_2Co_2Gd]ClO_4 \cdot 2CHCl_3 \cdot 4H_2O$.

Table S1. Details of the data collection and refinement parameters for **1**.

	1
Empirical formula	C ₁₄₂ H ₁₈₉ Cl ₉ Co ₉ N ₁₈ O ₉ P ₃
Formula weight	3394.48
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	<i>P</i> -1
Unit cell dimensions	$a = 18.446(5)$ $\alpha = 69.974(5)^\circ$ $b = 21.371(5)$ $\beta = 83.293(5)^\circ$ $c = 25.362(5)$ $\gamma = 64.700(5)^\circ$
Volume	8487(3) Å ³
Z	2
Density (calculated)	1.328 mg/mm ³
Absorption coefficient	1.086 mm ⁻¹
F(000)	3512.0
Crystal size	0.074 × 0.070 × 0.068 mm ³
Index ranges	-14 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 16 -17 ≤ <i>l</i> ≤ 20
Reflections collected	17701
Independent reflections	8698 [<i>R</i> (int) = 0.0385]
Absorption correction	Empirical
Max. and min. transmission	0.929, 0.923
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	8698/933/1657
Goodness-of-fit on <i>F</i> ²	1.137
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.1038, <i>wR</i> ₂ = 0.3158
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1151, <i>wR</i> ₂ = 0.3387
Largest diff. peak and hole	1.42/-0.95 e Å ⁻³

Table S2. Comparison table between trinuclear motif of **1**, $[\text{Co}_3(3,5\text{-DMPz})_4(3,5\text{-DMPzH})_2]$ and $[\text{P}(\text{S})\{\text{N}(\text{Me})\text{N}=\text{CH}-\text{C}_6\text{H}_4\text{-}o\text{-}\text{O}\}_3]_2\text{Co}_3$.

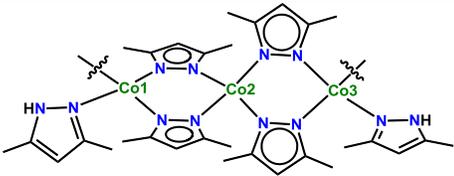
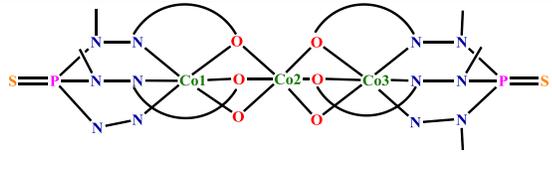
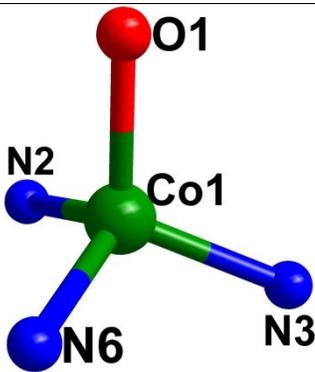
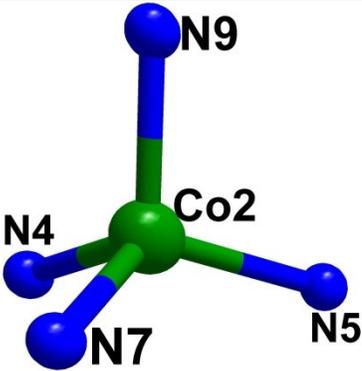
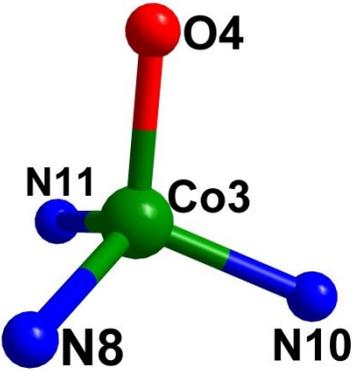
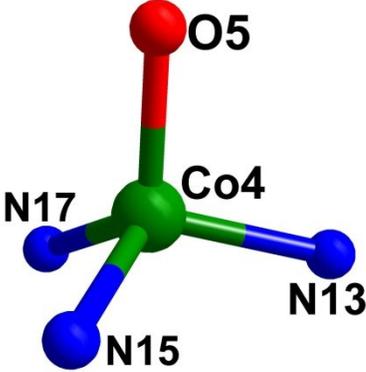
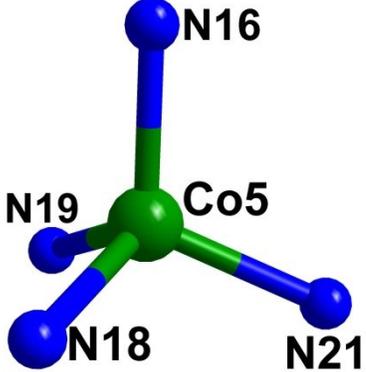
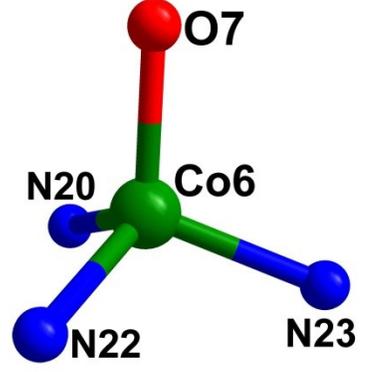
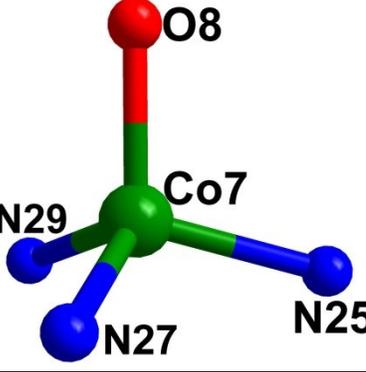
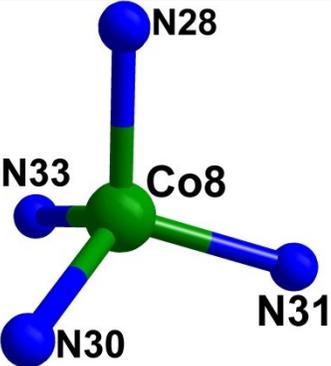
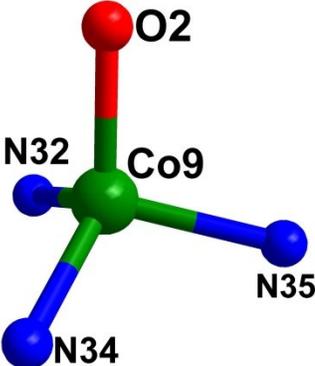
			
Co1---Co2	3.6 Å	Co1---Co2	2.88 Å
Co2---Co3	3.6 Å	Co2---Co3	2.88 Å
Co1---Co3	7.2 Å	Co1---Co3	5.76 Å
Co1---Co2---Co3	172.26°	Co1---Co2---Co3	176.66°

Table S3. Coordination geometries, bond distances (Å) and bond angles (°) of **1**.

	Bond distances (Å)		Bond angles (°)	
 <p style="text-align: center;">Tetrahedral</p>	Co1-N2	2.061(15)	O1-Co1-N2	104.2(5)
	Co1-N3	1.997(12)	N6-Co1-N2	115.2(5)
	Co1-N6	1.951(12)	N6-Co1-N3	109.2(5)
	Co1-O1	1.948(11)	O1-Co1-N3	114.1(5)
			O1-Co1-N6	107.5(5)
			N3-Co1-N2	106.7(5)
 <p style="text-align: center;">Tetrahedral</p>	Co2-N9	1.974(13)	N4-Co2-N9	113.8(5)
	Co2-N4	1.967(11)	N5-Co2-N4	109.3(5)
	Co2-N5	1.961(12)	N4-Co2-N7	101.9(5)
	Co2-N7	1.980(13)	N5-Co2-N9	103.7(5)
			N9-Co2-N7	110.1(5)
			N5-Co2-N7	118.5(5)
 <p style="text-align: center;">Tetrahedral</p>	Co3-N11	2.055(15)	O4-Co3-N10	109.3(5)
	Co3-N10	1.961(12)	N8-Co3-N11	113.1(5)
	Co3-N8	1.949(14)	N8-Co3-N10	108.6(5)
	Co3-O4	1.925(12)	O4-Co3-N11	104.7(5)
			O4-Co3-N8	113.9(5)
			N10-Co3-N11	106.9(6)

 <p style="text-align: center;">Co4 Tetrahedral</p>	<p>Co4-N15 2.001(13)</p> <p>Co4-N17 1.970(14)</p> <p>Co4-N13 2.000(17)</p> <p>Co4-O5 1.921(13)</p>	<p>N13-Co4-N15 114.8(6)</p> <p>O5-Co4-N15 102.8(5)</p> <p>O5-Co4-N17 121.1(5)</p> <p>N17-Co4-N13 106.4(6)</p> <p>N17-Co4-N15 107.5(6)</p> <p>O5-Co4-N13 104.7(6)</p>
 <p style="text-align: center;">Co5 Tetrahedral</p>	<p>Co5-N18 2.003(15)</p> <p>Co5-N21 1.975(13)</p> <p>Co5-N16 1.938(13)</p> <p>Co5-N19 2.026(14)</p>	<p>N16-Co5-N21 113.1(5)</p> <p>N21-Co5-N19 106.8(6)</p> <p>N18-Co5-N19 107.9(6)</p> <p>N16-Co5-N19 111.6(6)</p> <p>N16-Co5-N18 108.7(6)</p> <p>N21-Co5-N18 108.5(6)</p>
 <p style="text-align: center;">Co6 Tetrahedral</p>	<p>Co6-N23 2.010(16)</p> <p>Co6-N20 1.968(15)</p> <p>Co6-N22 1.981(13)</p> <p>Co6-O7 1.940(12)</p>	<p>O7-Co6-N20 110.2(5)</p> <p>N20-Co6-N23 110.6(6)</p> <p>N20-Co6-N22 108.8(6)</p> <p>O7-Co6-N23 109.0(6)</p> <p>N22-Co6-N23 105.6(6)</p> <p>O7-Co6-N22 112.6(5)</p>
 <p style="text-align: center;">Co7 Tetrahedral</p>	<p>Co7-N25 2.014(13)</p> <p>Co7-N29 1.971(12)</p> <p>Co7-N27 1.958(13)</p> <p>Co7-O8 1.936(11)</p>	<p>N27-Co7-N29 109.3(5)</p> <p>O8-Co7-N29 106.8(5)</p> <p>O8-Co7-N27 115.6(5)</p> <p>N27-Co7-N25 104.9(5)</p> <p>N29-Co7-N25 114.7(5)</p>

Tetrahedral		O8-Co7-N25 105.7(5)
 <p style="text-align: center;">Tetrahedral</p>	<p>Co8-N33 1.972(13) N31-Co8-N28 107.4(5)</p> <p>Co8-N31 1.953(13) N31-Co8-N30 111.8(5)</p> <p>Co8-N30 1.972(12) N31-Co8-N33 109.0(6)</p> <p>Co8-N28 2.003(13) N33-Co8-N28 107.9(5)</p> <p>N33-Co8-N30 111.2(5)</p> <p>N30-Co8-N28 109.4(5)</p>	
 <p style="text-align: center;">Tetrahedral</p>	<p>Co9-N34 1.970(14) O2-Co9-N34 120.7(5)</p> <p>Co9-N35 2.017(13) O2-Co9-N32 106.0(5)</p> <p>Co9-N32 1.996(12) O2-Co9-N35 102.7(5)</p> <p>Co9-O2 1.913(11) N34-Co9-N32 110.7(5)</p> <p>N34-Co9-N35 103.6(5)</p> <p>N32-Co9-N35 113.1(5)</p>	