Table II. The Experimental and Calculated Values for the Unit Cell and Atom Positional Parameters of the CuO, La_2O_3, and La_2CuO_4 Crystals[a,b]

CuO[15] monoclinic ($C2/c$)	La_2O_3[16] trigonal ($P\bar{3}ml$)	La_2CuO_4[1h] orthorhombic ($Cmca$)	La_2CuO_4 tetragonal ($I4/mmm$)
a = 4.6837 (-0.0321)	a = 3.930 (-0.029)	a = 5.3562 (-0.0078)	a = 3.7945
b = 3.4226 (-0.0644)	c = 6.120 (0.196)	b = 13.1669 (0.1015)	c = 13.1205
c = 5.1288 (0.0233)	z(La) = 0.235 (0.012)	c = 5.3990 (0.0129)	z(La) = 0.3633
β = 99.54 (-1.82)	z(O) = 0.630 (0.032)	y(La) = 0.3613 (0.0011)	z(O2) = 0.1827
z(O) = 0.4184 (0.0065)		z(La) = 0.0061 (0.0018)	
		y(O1) = 0.0070 (0.0056)	
		y(O2) = 0.1842 (-0.0007)	
		z(O2) = -0.0336 (-0.0153)	

[a] Except for tetragonal La_2CuO_4, the experimental values are the numbers without parentheses. The numbers in the parentheses refer to the deviations of the calculated values from the corresponding experimental ones. [b] The cell parameters a, b, and c are in units of Å, and the angle β is in units of deg.

C values describe the crystal structures of CuO and La_2O_3 quite well.[19]

To evaluate the energetics associated with the T → O distortion in La_2CuO_4, we employ the WMIN program and calculate the crystal energy of La_2CuO_4 as a function of its unit cell and atom positional parameters on the basis of the atom–atom potentials generated by the B, ρ, and C values of Table I. As summarized in Table II, the crystal structure of orthorhombic La_2CuO_4 is very well reproduced by the present atom–atom potential calculations.[19] Under the space group $Cmca$,[1h] the crystal structure of La_2CuO_4 is calculated to remain orthorhombic [i.e., the z(La), y(O1), and z(O1) values are nonzero], although this space group does not prevent La_2CuO_4 from becoming tetragonal. Also listed in Table II are the optimum unit cell and atom positional parameters of tetragonal La_2CuO_4, calculated by imposing the space group $I4/mmm$, which are very close to the unit cell and atom positional parameters of tetragonal $La_{1.85}Ba_{0.15}CuO_4$ at room temperature.[1h] According to the optimum structures of orthorhombic and tetragonal La_2CuO_4 obtained by the present atom–atom potential calculations, La_2CuO_4 is more stable in the orthorhombic than in the tetragonal structure by 1.85 kcal/mol per formula unit La_2CuO_4. This small energy difference seems quite reasonable, given the small structural difference between the two structures. We now examine how the dopants M might affect the T → O distortion. The Sr^{2+} and Ba^{2+} cations are larger in ionic radius than the La^{3+} cation,[20] and, in average, the copper atoms of $La_{2-x}M_xCuO_4$ are in a higher oxidation state and hence are smaller in size than those of La_2CuO_4. In general, a larger cation gives rise to greater nonbonded repulsions and can be characterized by a larger B or ρ value in the nonbonded repulsion terms associated with the cation. To simulate the crystal structure of $La_{2-x}M_xCuO_4$, therefore, we perform the atom–atom potential calculations on orthorhombic La_2CuO_4 by increasing the B value for the $La^{3+}\cdots La^{3+}$ pair and decreasing that for the $Cu^{2+}\cdots Cu^{2+}$ pair. With such changes in the two values, La_2CuO_4 is calculated to be orthorhombic but "less orthorhombic" in that the z(La), y(O1), and z(O2) values become closer to zero. That is, the driving force for the T → O distortion is diminished in $La_{2-x}M_xCuO_4$, and thus the T → O distortion temperature would be lower in $La_{2-x}M_xCuO_4$ than in La_2CuO_4. Since the Ba^{2+} cation is larger in size than the Sr^{2+} cation,[20] the T → O distortion temperature would be lower in $La_{1.85}Ba_{0.15}CuO_4$ than in $La_{1.85}Sr_{0.15}CuO_4$. These predictions are all in agreement with experiments.[2b,6]

In summary, the T → O distortion in both La_2CuO_4 and $La_{2-x}M_xCuO_4$ is not driven by an electronic instability, such as a Peierls distortion but by the ionic interactions involving the La^{3+} ions (and the M^{2+} ions as well in the doped materials).

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(19) The calculated structures for CuO and orthorhombic La_2CuO_4 represent saddle points on the five- and eight-dimensional potential energy surfaces, respectively. With the present set of empirical potentials, minimum energy structures calculated for CuO and orthorhombic La_2CuO_4 are found physically meaningless.
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A Regioselective Mechanism for Mutagenesis and Oncogenesis Caused by Alkylnitrosourea Sequence-Specific DNA Alkylation[1]

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In the standard mechanism for alkylnitrosourea (ANU) alkylation of DNA in vitro and in vivo,[2] reactive intermediates formed hydrolytically in cytosol by the sequence ANU ⇌ $RCH_2N{=}N{-}OH \rightarrow RCHN_2 \rightleftharpoons RCH_2N_2^+ \rightarrow$ "RCH_2^+" are thought to react with DNA nucleophiles by direct displacement, a process that should give a random distribution of products. Indeed, the "S_N2" reagents dimethylsulfate and 2-chloroethyl-(methylsulfonyl)methane sulfonate give random, nonsequence specific products at N_7-guanine (N_7-dG) in pBR-322 DNA.[3] Yet the powerful mutagenic[4] and oncogenic[5] properties of the ANUs 1-methyl-(MNU) and 1-ethyl-1-nitrosourea (ENU) are related to site- and sequence-specific alkylation of O^6-dG_2 in a 5′-dGdGdN-3′ DNA codon, where dN is any base; neither N_7-dG_1 nor O^6-dG_1 is alkylated.[3-5] Sequence-specific reactions of ANUs

* Correspondence should be addressed to the author, c/o The Editorial Office, 1360 Ninth Avenue, Suite 210, San Francisco, CA 94122.
(1) Supported in part by NIH Program Project Grant CA-13525.
(2) See Lown, J. W.; Chauhan, S. M. S.; Koganty, R. R.; Sapse, A.-M. *J. Am. Chem. Soc.* **1984**, *106*, 6401-6408.
(3) Hartley, J. A.; Gibson, N. W.; Kohn, K. W.; Mattes, W. B. *Cancer Res.* **1986**, *46*, 1943-1947. 1-(2-Chloroethyl)-1-nitrosoureas (CENUs) give sequence-specific DNA alkylation products at N_7-dG. These authors reported no site-specific alkylation at N_7-dG for treatment with 5 mM ENU, but this high concentration may saturate available alkylation sites[6b] and mask sequence-specific alkylation.
(4) The dAdT (82%) or dTdA (71%) mutations in the plasmid-carried *gpt* gene of *E. coli* treated with MNU and ENU are caused by sequence-specific alkylation of O^6-dG_2 in the codon 5′-$dG_1dG_2dN_3$-3′ (Richardson, K. K.; Richardson, F. C.; Crosby, R. M.; Swenberg, J. A.; Skopek, T. R. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 344-348).
(5) Activated Ha-*ras*-1 oncogenes in rat mammary tumors induced by MNU in vivo contained dG_1-MeO^6-dG_2 to dAdT mutations in the sequence 5′-$dG_1dG_2dN_3$-3′ (dN = dA or dC) (Zarbl, H.; Sukumar, S.; Arthur, A. V.; Martin-Zanca, D.; Barbacid, M. *Nature (London)* **1985**, *315*, 382-385).

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Scheme I

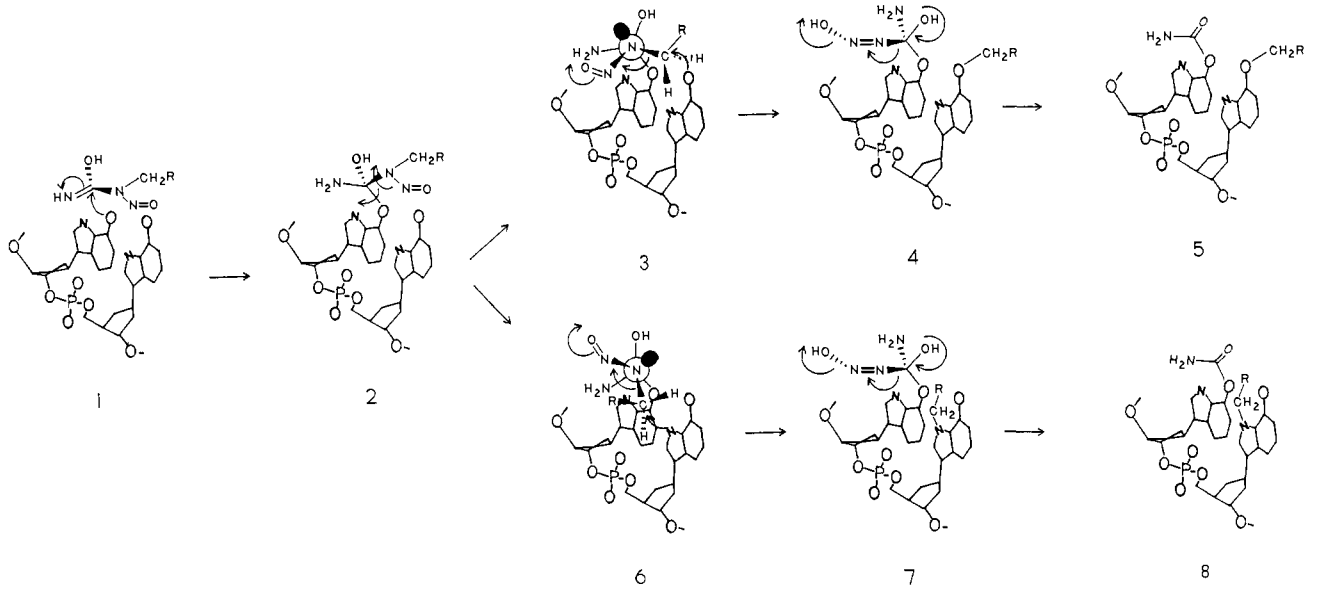

Table I. Relative Yields of Alkyl-N_7-dG for Treatment of DNA with Ethereal Diazoalkanes and Other Alkylating Agents

agent					
CH_2N_2	$MeCHN_2$	MMS	EMS	MNU	ENU
81[a]	74[a]	81[b]	58[b]	66[b]	11[b]
		86[c]	73[c]		

[a] From ref 11. [b] From ref 17. [c] From ref 16.

may occur through an intermediate covalently bound to the major groove of DNA. A regioselective mechanism[6a,b] that may explain the kinetics and sequence-specific products for ANUs is proposed here for a 5′-dGdG-3′ pair in B-DNA (Scheme I; only N_7 and O^6 are shown).[6c] It is probable that the imidourea[6a] and not parent ANU adds to O^6-dG_1 to form the tetrahedral intermediate **2**. In a first-order intramolecular reaction, RCH_2- may be displaced by either O^6-dG_2 (**3**) or N_7-dG_2 (**6**) to give **4** and **7** that collapse to **5** and **8**, respectively. Hydrolysis of the carbamates yields alkylated DNA.[7]

There is evidence that carbocation-like hydrolysis products from ANUs are not the primary DNA alkylating species. Alkylation of calf-thymus DNA by *n*-propylnitrosourea (PNU) is strictly first order, and k_{obsd} (0.090 min^{-1} for 0.1 and 1.0 mM) is threefold greater than the rate constant for hydrolysis (k_{obsd} = 0.029 min^{-1}).[8] This profile is incompatable with an overall reaction in which hydrolysis of an ANU to carbocations or their precursors is rate-limiting[2] but is consistent with Scheme I.

Electrophilic addition of "RCH_2^+" to DNA is not a primary pathway because *n*-propyl[8] and *n*-butyl[9] groups from the respective ANU are transferred essentially intact to O^6-dG.[10] Moreover, while *exogenous* $RCHN_2$ alkylates DNA[11]—presumably through $RCH_2N_2^+$—and intermediates from the hydrolysis of MNU[12a] and exogenous CH_2N_2[12b] ($t_{1/2}$ of 1.3 s in 60:40 aqueous THF[13]) undergo H–D exchange reactions in D_2O–phosphate buffer, pH 7.2, the [^{3}H]methyl[^{14}C] of MNU is transferred intact to DNA nucleophiles.[14,15] In addition, the fraction of Et-N_7-dG in DNA treated with ethereal $MeCHN_2$[11] is similar to that for the "S_N2" reagent ethyl methanesulfonate (EMS)[16,17] but not to that for ENU[17] (Table I), and fractions of products and the methyl/ethyl ratios for treatment of DNA with MNU and ENU and for methyl methanesulfonate (MMS) and EMS are clearly different (Table II).[18] Therefore, neither $RCH_2N_2^+$ nor $RCH_2N{=}N{-}OH$ is a

Table II. Relative Yields of Alkylation at the N_7 and O^6 Positions of Guanine for Treatment of DNA with Various Alkylating Agents[a]

				Me/Et	
agent	N_7	O^6	N_7/O^{6a}	N_7	O^6
MNU	66	5.4	12.3		
				6.0	0.57
ENU	11	9.5	1.16		
MMS	81	0.3	270		
				1.4	0.014
EMS	58	2.1	27.8		

[a] In pmol/μmol DNA, from ref 17. The ratio of N_7 to O^6 is related to the relative nucleophilicities; see: Pullman and Pullman, ref 15.

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(7) DNA treated with [^{14}C]carbonyl MNU, ENU, and PNU has no bound radioactivity, but polylysine, polyhistidine, and histone do, presumably as the more stable ureas[6a] (Morimoto, K.; Tanaka, A.; Yamaha, T. *Gann* **1979**, *70*, 693–698). [^{14}C]labeled R—NHCON(N=O)Et—Cl are covalently bound to DNA (Nishigaki, T.; Tanaka, M. *Chem.-Biol. Interact.* **1985**, *56*, 213–224) and albumin (Weinkam, R. J.; Liu, T.-Y. J.; Lin, H.-S. *Chem.-Biol. Interact.* **1980**, *31*, 167–177).

(8) Calculated from data of Morimoto et al. (Morimoto, K.; Takaka, A.; Yamaha, T. *Carcinogenesis* **1983**, *4*, 1455–1458). At pH 7, 37 °C, k_{obsd} are 0.087, 0.051, and 0.095 min^{-1} for 0.1, 0.5, and 1.0 mM PNU, respectively. DNA alkylation by PNU is not *pseudo*-first order.

(9) Saffhill, R. *Carcinogenesis* **1984**, *5*, 621–625.

(10) While some isopropyl and *sec*-butyl adducts are formed, indicating some cationic character in the reaction, the fractions of rearranged products at O^6- or N_7-dG are lower than the fractions of rearranged alcohols from hydrolysis of the respective ANUs.[8,9]

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(14) Lawley, P. D.; Shah, S. A. *Chem.-Biol. Interact.* **1973**, *7*, 115–120. Proton abstraction may be slowed by a very high primary isotope effect.[12a] Nonetheless, the reaction occurs with facility. Deuteriated alkyl groups of bis-alkylnitrosamines are transferred intact to DNA (R = Me: Lijinsky, W.; Ross, A. E.; Loo, J. *Nature (London)* **1968**, *218*, 1174–1175. R = Et: Ross, A. E.; Keefer, L.; Lijinsky, W. *J. Natl. Cancer. Inst.* **1971**, *47*, 789–795).

(15) The powerful mutagen *N′*-methyl-*N*-nitro-*N′*-nitrosoguanidine (MNNG) is a CH_2N_2 precursor (upon treatment with 40% aqueous KOH (Feiser, L.; Feiser, M. L. *Reagents for Organic Chemistry*; Wiley: New York, 1967; p 192)) with an hydrolysis profile similar to ANUs and CENUs at neutral pH (Lawley, P. D.; Thatcher, C. J. *Biochem. J.* **1970**, *116*, 693–707) that does not alkylate guanosine but readily alkylates poly (G), poly (G.C), and DNA (discussed in Pullman, B.; Pullman, A. In *Carcinogenesis: Fundamental Mechanisms and Environmental Effects*; Pullman, B., Ts'o, P. O. P., Gelboin, H., Eds.; D. Reidel: New York, 1980; pp 55–66), which rules out CH_2N_2 as the alkylating intermediate. DNA secondary structure is necessary for these alkylation reactions.

(16) (a) Lawley, P. D.; Brookes, P. *Biochem. J.* **1963**, *89*, 127–138. See, also: (b) Swenson, D. H.; Lawley, P. D. *Biochem. J.* **1978**, *171*, 575–587.

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(18) N_7/O^6-dG ratios for PNU[8] and *n*-butylnitrosourea[9] are essentially the same as the ratio for ENU.

primary intermediate in ANU alkylation of DNA.

The tetrahedral precursor lesion **2** is an attractive alternative to carbocation-like intermediates, and the sequence in Scheme I provides a self-consistent, regioselective mechanism for the mutagenic and oncogenic DNA alkylation reactions of ANUs. Environmental mutagens and carcinogens such as alkylnitrosamines, or their in situ metabolites, may have a similar mechanism of action.

Acknowledgment. Collaborative studies with Dr. Thomas P. Brent led to the mechanism proposed here. I thank several of the referees for insightful comments that improved the manuscript.

Metal-Metal Bonds Involving Actinides. Functionalization of Activated C-H Bonds and Unusual Oligomerization Chemistry Mediated by a Thorium-Ruthenium Complex

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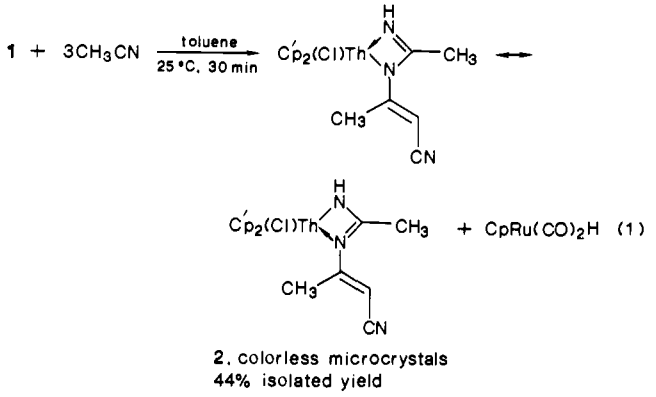
Actinide-to-transition metal bonds[1-3] represent a new type of heterobimetallic[4,5] linkage, the chemistry of which remains largely unexplored. Such functionalities offer the potential of cooperative chemistry involving strong metallonucleophiles and metalloelectrophiles. We report here two unusual $Cp'_2Th(Cl)Ru(Cp)(CO)_2$ (**1**, Cp' = η^5-$(CH_3)_5C_5$; Cp = η^5-C_5H_5)-mediated transformations involving both facile heterobimetallic C-H functionalization and actinide-centered substrate insertion/oligomerization. In the case of acetonitrile, the result is a novel diazathoracyclobutene (amidinate).

Complex **1** undergoes rapid, quantitative reaction (by NMR) with acetonitrile (no detectable intermediates) to yield **2** (eq 1)



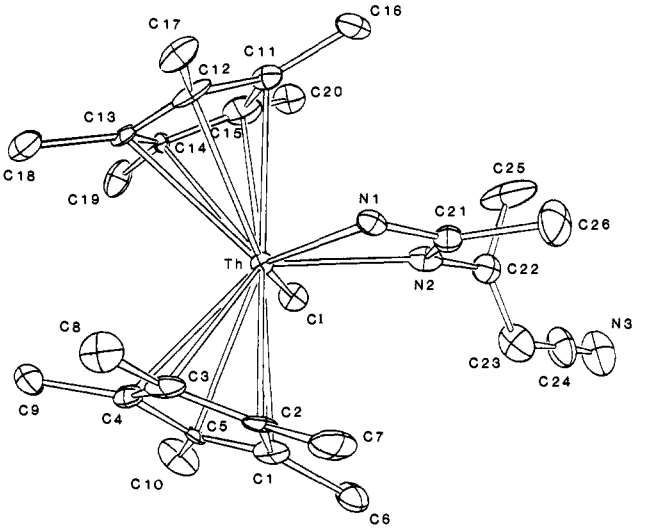


Figure 1. Perspective drawing of the molecular structure of $Cp'_2Th(Cl)(C_6H_8N_3)$ (**1**). The shapes of the ellipsoids correspond to 30% probability contours of atomic displacement. Individual bond lengths (Å) and angles (deg) of interest: Th-N1, 2.46 (1); Th-N2, 2.46 (1); N1-C21, 1.29 (2); N2-C21, 1.32 (2); C21-C26, 1.50 (2); N2-C22, 1.43 (2); C22-C23, 1.36 (3); C23-C24, 1.39 (3); C24-N3, 1.17 (3); N1-Th-N2, 52.2 (5); Th-N1-C21, 98 (1); Th-N2-C21, 97 (1); N1-C21-N2, 112 (2); Th-N2-C22, 140 (1).

and $CpRu(CO)_2H$ (by NMR[6]). The structural assignment follows from $^1H/^{13}C$ NMR,[7] IR[7,8] (ν_{NH} = 3345, $\nu_{C\equiv N}$ = 2203 cm^{-1}), MS,[7] elemental analysis,[7] and X-ray diffraction.[9] The latter data (Figure 1) reveal an unexceptional[10] Cp'_2ThCl fragment (∠Cp' centroid-Th-Cp' centroid = 135.5°; Th-Cl = 2.697 (4) Å; Th-C(ring) = 2.80 (2, 1, 4, 10)[11] Å) and a bidentate amidinate[12] ligand. The observed equality of Th-N1, Th-N2, the near equality of N1-C21, N2-C21, and the coplanarity (to within

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(7) ^1H NMR (C_6D_6, 22 °C) δ 5.10 (br s, 1 H, NH), 4.13 (s, 1 H, CH), 2.23 (s, 3 H, CH_3), 1.87 (s, 30 H, Cp'_2Th), 1.25 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6, 20 °C) δ 172.2 (s, *C*-CH_3), 166.5 (s, *C*-CH_3), 124.6 (s, Cp' ring), 118.1 (s, C≡N), 86.54 (d, J_{CH} = 169 Hz, CH), 23.76 (q, J_{CH} = 126 Hz, C-*C*H_3), 21.89 (q, J_{CH} = 126 Hz, C-*C*H_3), 11.46 (q, J_{CH} = 127 Hz, Cp'-*C*H_3); IR (Nujol, cm^{-1}) 3345 s, 2203 m, 1608 sh, 1594 m, 1310 s, 1255 s, 1141 m, 1020 m, 820 m, 565 w; MS, 15 eV [*m/e* (rel abundance), assignment] 659 (2), $Cp'_2Th(Cl)(C_6H_8N_3)^+$; 624 (1), $Cp'_2Th(C_6H_8N_3)^+$; 537 (1), Cp'_2ThCl^+; 524 (100), $Cp'Th(Cl)(C_6H_8N_3)^+$. Anal. Calcd for $C_{26}H_{38}N_3ClTh$: C, 47.31; H, 5.80; N, 6.37. Found: C, 47.19; H, 5.86; N, 6.70.

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(9) Crystal data: $C_{26}H_{38}N_3ClTh$; M = 660.1; orthorhombic, space group $P2_12_12_1$ (No. 19) a = 15.139 (5) Å, b = 15.766 (4) Å, c = 10.930 (3) Å at -120 °C; V = 2609 (2) Å^3; Z = 4; d_{calcd} = 1.68 g/cm^3. The structure was solved by Patterson and Fourier techniques and refined to R(F) and R_w(F) of 0.044 and 0.047, respectively, with use of 2181 absorption-corrected reflections with $I > 3\sigma(I)$ measured on an Enraf Nonius CAD4 diffractometer (Mo Kα radiation, λ = 0.71069 Å, $2\theta_{max}$ = 55°). A full description of the structure determination is included in the Supplementary Material.

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(11) The first number in parentheses following an averaged value of a bond length or angle is the estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

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