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Cryptands with Large Cavity Lengths Over 16 Å and N_8O_6Hetero-donors: Template Macrobicyclization and Structure of a Binuclear Copper(I) Cryptate

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Hetero-tritopic N_8O_6 cryptands L^1 and L^2 were synthesized *via* 2 +3 silver(I) template Schiff-base macrobicyclization of tris(2-aminoethyl)amine and tris(3-aminopropyl)amine with 4,4′-methylenedioxy-dibenzaldehyde, respectively. The resulting binuclear silver(I) cryptates $[Ag_2L^1](ClO_4)_2$ (1) and $[Ag_2L^2](ClO_4)_2$ (2) were characterized by various methods (elemental analyses, IR, UV-Vis, ^1H and ^{13}C NMR, and FAB mass spectra). The binuclear copper(I) cryptate $[Cu_2L^1I(BF_4)_2 \bullet DMF \bullet EtOH \bullet H_2O$ (3) was synthesized by transmetallation with 1 and studied by spectroscopic and X-ray structural analyses. It crystallizes in the monoclinic, space group $P2_1/n$ with $a = 16.088(5)$, $b = 11.941(4)$, $c = 34.08(1)$ Å, $\beta = 91.69(2)°$, $Z = 4$. $d = 1.41\,g\,cm^{-3}$. $R_1 = 0.117$, $wR_2 = 0.111$ (on 3859 observed with $I > 2\sigma(I)$). The bicopper(I) cryptate looks like a twisted elongated ellipsoid, possessing cavity length 16.4Å and Cu(1)···Cu(2) separation 12.132(5) Å. The two Cu(I) centers have similarly high stability towards oxidation. The cryptate does not show any reactivity or inclusion towards 4,4′-bipyridine, imidazole, N_3^-, Na^+, K^+ and NH_4^+, mainly due to the highly effective distorted tetrahedron coordination around each Cu(I) enter and twisting among the three bridging-chains in the cryptand.

INTRODUCTION

There is considerable current attention on architecture of three-dimensional macro-bicyclic or -polycyclic receptors with large cavities and multiple recognition [1-4], which form mono-, bi- or poly-nuclear metal complexes with regard to their potentials as supramolecular catalyst [5, 6], metalloenzyme models [7], and molecular devices [8]. Using Schiff-base macrobicyclization [9], we have constructed a series of polyaza cryptands and cryptates with large and flexible cavities, which exhibit interesting conformation isomerism (from *cis*-basket [10] to trans-twisted shapes [11]) and poly-metal inclusion (poly-nuclear silver(I) and copper(I) helical cryptates [12]). We describe herein two novel N_8O_6 heterotritopic cryptands L^1 and L^2 (Fig. 1) with nanosized cavities, covering silver(I)-template Schiffbase syntheses and spectroscopic and

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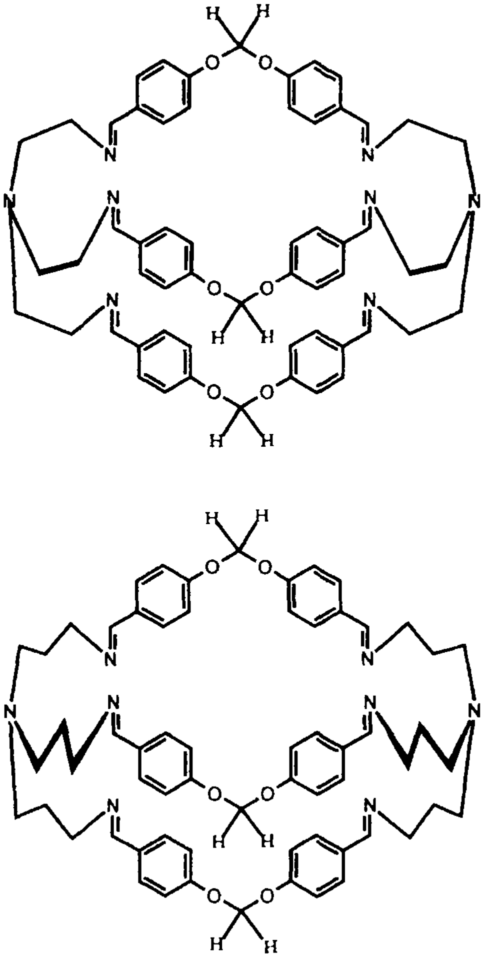

FIGURE 1 N_8O_6 hetero-tritopic cryptands L^1 (top) and L^2 (bottom).

structural characterization. The structure of the binuclear copper(I) cryptate of L^1 shows the cryptand has a cavity length of over 16 Å and an intermetal distance of over 12 Å. To our knowledge, only a few cryptands exist with cavity lengths of over 15Å. An example binuclear copper(I) cryptate with metal-metal separation of over 10Å resulting from Schiff-base macrobicyclization has been characterized by X-ray structural analyses [9, 13-15]. Recently, several Schiff-base and resulting amine cryptands with large cavities have been reported with only spectroscopic characterization [16-19].

EXPERIMENTAL SECTION

Tripodal polyamines tris(2-aminoethyl)amine (tren) and tris(3-aminopropyl)amine (trpn) were prepared by the methods described in our previous publications [10-12]. 4,4′-methylenedioxydibenzaldehyde was prepared by a literature method [20] and identified by elemental analysis and NMR spectra.

IR and UV-Vis spectra were recorded on a Magna FT IR 750 spectrophotometer in the range 4000-400 cm^{-1} (KBr pellets) and on a Shimadzu UV 3000 spectrophotometer at room temperature, respectively. Positive FAB mass spectra were obtained on a VG-ZAB-HS spectrometer, *m*-nitrobenzyl (NBA) used as matrix. ^1H and ^{13}C NMR spectra was carried out on a Varian Unity 500 spectrometer at room temperature, TMS used as the internal standard. Cyclic voltammogram was measured on a Hokoto HAB-151 electrochemical instrument in acetonitrile solution (0.1 mol dm^{-3} NBu_4BF_4) of the bicopper(I) cryptate. A standard three-electrode cell was used comprising platium disk working, platium wire auxiliary and Ag/AgCl reference electrodes.

$[Ag_2L^1](ClO_4)_2$ (**1**) To a stirred solution of $AgNO_3$ (0.510 g, 3 mmol) and 4,4′-methylenedioxybenzaldehyde (0.768 g, 3 mmol) in 100 cm^3 absolute ethanol was added dropwise a solution of tren (0.292 g, 2 mmol) in 50 cm^3absolute alcohol. After stirring for 3h, an excess of sodium perchlorate (0.7 g, ca. 5 mmol) was added to the mixture. Then a white precipitate was isolated and collected by filtration; washing with alcohol, followed by recrystallization from acetonitrile, yielded 1.1 g of **1** (74%). ^1H NMR (500 MHz, CD_3CN, TMS) $\delta = 8.53$ (s, 6H, HC = N), 7.85, 7.84 (d, 12H, Ph-H, ^3J(H, H) = 8.5 Hz), 7.04, 7.02 (d, 12H, Ph-H, ^3J(H, H) = 8.5 Hz), 5.83 (s, 6H, OCH_2O), 3.74 (m, 12H, CH_2N(imino)), 2.95 (m, 12H, CH_2N(bridge-head)). ^{13}C NMR $\delta = 164.6$ (C = N), 160.4 (PhC(1)), 155.9 (Ph-C(4)), 130.7, 130.2 (Ph-C(2,6)), 11.7 (Ph-C(3,5)), 91.0 (OCH_2O), 59.7, 55.9 (CH_2N(imino)), 36.6 (CH_2N(bridgehead)). FAB-MS m / z 1267 (M-ClO_4), 1169 (M-2ClO_4), 1058 (M-Ag-2ClO_4). IR(KBr, cm^{-1}) 2942, 2902, 2838, 1645s (C = N), 1604, 1508, 1211, 1089s (ClO4), 1014, 835, 624. UV-Vis (MeCN) [λ_{max} (nm) (ε(1 mol^{-1} cm^{-1})]: 280 (42 300). Anal. calc. for $C_{57}H_{60}Ag_2Cl_2N_8O_{14}$: C, 50.05; H, 4.42; N, 8.19. Found: C, 50.23; H, 4.15; N, 8.52.

[Ag_2L^2](ClO_4)$_2$ (**2**) A similar procedure to the above afforded the complex with L^2 obtained as yellowish powder of **2**, yield 78% ^{1}H. NMR (500 MHz, CD_3CN, TMS) δ = 8.39 (s, 6H, HC = N), 7.86, 7.84(d, 12H, Ph-H, ^3J(H,H) = 8.5 Hz), 6.60, 6.59 (d, 12H, Ph-H, ^3J(H,H) = 8.5 Hz), 5.50 (s, 6H, OCH_2O), 3.84 (m, 12H, CH_2N(imino)), 3.29 ~ 2.71 (m, 12H, CH_2N (bridgehead)), 2.21 (m, 12H, CH_2). ^{13}C NMR δ = 165.0 (C = N), 160.6 (Ph-C(1)), 136.6 (PhC(4)), 130.9, 129.4 (Ph-C(2,6)), 117.2 (Ph-C(3,5)), 91.9 (OCH_2O), 66.4 (CH_2N(imino)), 59.9 (CH_2N(bridgehead)), 28.9, 25.3, 24.5 (CH_2). FAB-MS m / z 1352(M-$C1O_4$), 1143 (M-Ag-2ClO_4), 1036 (M-2Ag-2ClO_4). IR (KBr, cm^{-1}): 3072, 2908, 2848, 1639s (C = N), 1604, 1508, 1456, 1307, 1218, 1170, 1089s(ClO_4), 1004, 835, 723, 622. UV-Vis (MeCN) [λ_{max}(nm) (ε(1 $mol^{-1}cm^{-1}$)]: 278 (40 600). Anal. calc. for $C_{63}H_{72}Ag_2Cl_2N_8O_{14}$: C, 52.12; H, 5.00; N, 7.72. Found: C, 52.42; H, 4.83; N, 7.85.

[Cu_2L^1 [(BF_4)$_2$ • DMF • EtOH • H_2O (**3**) An excess of $Cu(MeCN)_4BF_4$(0.16 g, 0.5 mmol) was added to a stirred solution of **1** (0.15 g, 0.1 mmol) in 1:1 MeCN−EtOH (10 cm^3), a yellowish precipitate formed after several min. and was separated by filtration. The precipitate was dissolved in ethanol mixed with drops of DMF and the insoluble material was removed by filtration. After slow diffusion of ethyl ether into the filtrate for a week at room temperature, yellowish crystals of **3** suitable for X-ray single crystal diffraction were obtained, yield 64%. ^{1}H NMR (500 MHz, CD_3CN, TMS) δ = 8.45 (s, 6H, HC = N), 8.24, 8.22 (d, 12H, Ph-H, ^3J(H, H) = 8.5 Hz), 6.74, 6.72 (d, 12H, Ph-H, ^3J(H, H) = 8.5 Hz), 5.59 (s, 6H, OCH_2 O), 3.79 (m, 12H, CH_2N(imino)), 3.10, 3.09 (m, 12H, CH_2N(bridgehead)); 7.9 (s, HCO(DMF)), 2.90, 2.78 (d, NMe_2(DMF)), 3.4 (m, CH_2(EtOH)), 1.2 (m, Me(EtOH)). IR (KBr, cm^{-1}): 3425w, 3041, 2918, 2860, 1666, 1633s, (C = N), 1606, 1577, 1512, 1311, 1228, 1178, 1086s, 1018, 933, 899, 827, 735, 623. UV-Vis (MeCN) [λ_{max} (nm) (ε(1mol^{-1}cm^{-1})]: 282 (48000), 350(12 900). Anal. calc. for $C_{62}H_{75}B_2Cu_2F_8N_9O_9$: C, 53.53; H, 5.43; N, 9.06. Found: C, 54.21; H, 4.91; N, 9.54.

Safety Notes

Perchiorate salts of metal complexes with organic compounds are potentially explosive. Only a small amount of material should be prepared and this should be handled with great caution.

Crystallographic Analysis of 3

Details of crystal data and data collection information are given in Table I.

A yellowish pellet crystal coated with gel was mounted on a glass fiber and used for structure determination. The unit cell parameters were determined from least-squares refinement of the setting angles (9.98 < 6 < 10.80°) for 25 reflections.

TABLE I Crystallographic data for 3

Formula	$C_{62}H_{75}B_2Cu_2F_8N_9O_9$
Formula weight	1391.03
Space group	$P2_1/n$
a. Å	16.088(5)
b. Å	11.941(4)
c. Å	34.08(1)
β.°	91.69(2)
V.Å^3	6545(6)
Z	4
dcalc. g cm^{-3}	1.41
$F(000)$	2829
μ cm^{-1}	7.60
diffractometer	Enraf-nonius CAD 4
Approx. cyrstal size. nm	0.125 × 0.2 × 0.4
λ (Mo Kα), Å	0.71069
Temperature (K)	296(2)
No. of observed with $I > 2\sigma$	3859
No. of variables	847
R. wR	0.117; 0.111
Goodness of fit	2.00
Final $\Delta\rho$max. $\Delta\rho$min.eÅ^{-3}	0.85; −0.73

Using the ω-2θ scan technique (scan speed $<5.49° \min^{-1}$, scan width $= 1.20 + 0.35 \tan\theta$, $0 \le h < 19$, $0 \le k \le 14$, $-40 \le 1 \le 40$), unique reflections were collected to a maximum 2θ value of 49.9°. 3859 reflections with $I \ge 2\sigma(I)$ were used in the structural refinement. There was a linear decay during data collection, according to the intensities of three standard reflections (7, 3, 3; $-7, -2, 8$; $-4, -5, 5$) which were measured every 300 reflections (decay 11.2%). Decay and absorption correction ψ scans were applied to each data set (Rint = 0.024, Tmax = 1.00 and Tmin = 0.6748). The locations of copper atoms were determined by direct methods. The remaining non-hydrogen atoms were located through successive least-squares refinements on difference Fourier map using the TEXSAN(V2.1) structure solution package [21]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions. The weighting scheme was $w^{-1} = \sigma^2(F)$. All calculations were performed on a Micro-VAX 3100 computer. Further refinement is not accessible, owing to the rather poor data and highly disorder from the anions and solvents.

RESULTS AND DISCUSSION

The N_8O_6 hetero-tritopic cryptands L^1 and L^2 were synthesized by Ag(I)-template 2 + 3 Schiff-base condensation of tren and trpn with the methylenedioxy bridged dialdehyde in high yields, respectively. Elemental analyses and spectroscopic characterization are in agreement with the bimetal cryptate formulas. In their IR spectra, there is a very strong band at ca. $1640\,\mathrm{cm}^{-1}$, due to the stretching vibration of $C=N$, without bands assigned to aldehyde and primary amine groups from the starting materials. This confirms that formation of the Schiff-base is complete. The three cyptates have similar symmetrical resonance mode in their NMR spectra, showing that the three bridging chains in the cryptand L^1 or L^2 are equivalent and the binuclear metals are symmetrically bound in each site of the cryptand cavity. The FAB mass spectras of **1** gave the important peaks at m / z 1267, 1169 and 1058, assigned to the species $\{[Ag_2L^1](ClO_4)\}^+$, $[Ag_2L^1]^+$, and $[AgL^1]^+$ resulting from stepwise loss of ClO_4 and Ag atom, respectively; while the FAB mass spectras of **2** shows several important peaks at m / z 1352, 1143 and 1036 corresponding to the fragments $\{[Ag_2L^2](ClO_4)\}^+$, $[AgL^1]^+$, and $[L^2]^+$, respectively. It is noteworthy that no clearly resolved spectrum can be assigned to the free-metal ligand L^1, except the fragments resulting from the broken macrobicycle, indicating that binding between metal and cryptand in **1** is stronger than that in **2**. Further transmetallation with the copper(I) salt has also shown the different binding strength between copper(I) and cryptand. Upon treatment of the copper(I) salt (BF_4, ClO_4 or PF_6 anion) with **1** in acetonitrile, a yellowish preciptate formed during several minutes stirring at room temperature. The product is very air-stable, even if it is recrystallized in ethanol and DMF instead of acetonitrile, which is capable of stabilizing Cu(I) by coordination. However, when the copper(I) salt is mixed with **2** in acetonitrile under an inert atomsphere, a red colored solution formed but changed immediately into a blue colored solution. We have not obtained pure compound from the solution yet. The fact shows again that coordination between metal and the more flexible trpn-derived cryptand L^2 is quite weak. Consequently, silver(I) ion can readily oxidize copper(I) in the cavity. The efforts to extend the non-template macrobicyclization [9] to the syntheses of the two cryptands also failed, possibly attributed to the flexibility of 4, 4′-methylenedioxydibenzaldehyde and trpn, although they are very similar analogues to 4,4′-methylenedibenzaldehyde and tren, [9] respectively.

The structure of the cationic complex $[Cu_2L^1]^{2+}$of **3** is shown in Figure 2. Selected

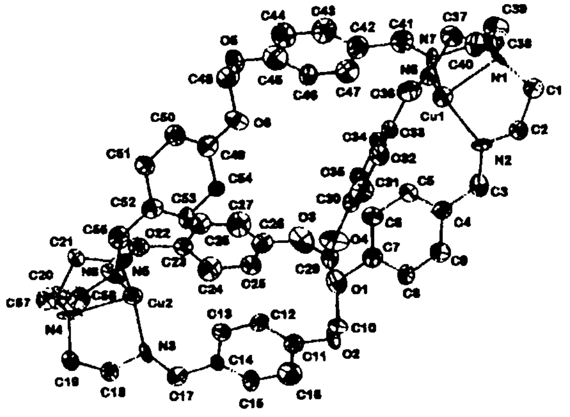

FIGURE 2 OETEP views of the cationic cryptate $[Cu_2L^1]^{2+}$ in 3 showing 50% probability thermal motion ellipsoid.

bond distances (Å) and angles (°) are listed in Table II.

Each copper ion in the binuclear cryptate is situated at a distorted tetrahedron composed of three imino nitrogens and a bridgehead tertiary nitrogen. Average distances of Cu —N(imino) and Cu —N(bridgehead) are 2.00(2) and 219(2)Å, respectively. The Cu atom lies near the base composed of three imino *N* donors but far away from the top (the bridgehead N atom) of the distorted tetrahedron, in keeping with the stronger bonding between Cu(I) and the soft, very low basicity, N(imino) atoms, but a weaker interaction between Cu(I) and the hard, more strongly basic tertiary nitrogens [24]. The average N —Cu —N angle (comprised of the bridgehead nitrogen, metal, and a imino nitrogen) is 84.5(7)°; while the average value of the three N —Cu —N angles (involving in a imino nitrogen, metal, and another imino nitrogen) is 119.1(7)°. There is a pseudo C_3-axis which runs through the two bridgehead nitrogens. The bond parameters are very similar to those of the reported binuclear copper(I) complexes with tren-derived Schiff-base macrobicyclic cryptands. [9, 22] The important cavity size of the cryptate is given as follows: cavity length (distance between the bridgehead nitrogens N(1) and N(4)) 16.4Å; internuclear separation (distance between Cu(1) and Cu(2)) 12.132(5)Å; distances between any two methylenedioxy bridges (OCH_2O) 8.95, 7.85 and 6.31Å, respectively; the dihedral angles between two benzene rings in each bridging-chain are 37.5, 60.33 and 109.33°, respectively. The three bridge chains in the cryptand are twisted with respect to one another due to the flexibility, different from the rigid-bridging tren-derived Schiff-base cryptates [9, 22]. Thus the dicopper(I) cryptate looks like a twisted, elongated ellipsoid; while the rigid analogues exhibit almost ellipsoidal conformations. It is noted that the average bond angle of the three methylenedioxy bridges (OCH_2O) is 114.7°, deviating from that at a normal tetra-

TABLE II Selected interatomic distances (Å) and angles (°) of 3

Cu(1) —N(1)	2.18(2)	Cu(2) —N(4)	2.19(2)
Cu(1) —N(2)	1.99(2)	Cu(2) —N(5)	1.97(2)
Cu(1) —N(6)	2.01(2)	Cu(2) —N(3)	1.98(2)
Cu(1) —N(7)	2.03(2)	Cu(2) —N(8)	2.02(2)
Cu(1)···Cu(2)	12.132(5)	N(1)···N(4)	16.4
N(2) —Cu(1) —N(6)	111.9(7)	N(5) —Cu(2) —N(3)	115.4(7)
N(2) —Cu(1) —N(7)	125.8(7)	N(5) —Cu(2) —N(8)	115.1(7)
N(2) —Cu(1) —N(1)	85.6(7)	N(5) —Cu(2) —N((4)	84.1(8)
N(6) —Cu(1) —N(7)	119.5(7)	N(3) —Cu(2) —N(8)	126.8(7)
N(6) —Cu(1) —N(1)	83.7(7)	N(3) —Cu(2) —N(4)	86.5(7)
N(7) —Cu(1) —N(1)	84.0(7)	N(8) —Cu(2) —N(4)	83.2(7)
C(7) —O(1) —C(10)	118(2)	C(10) —O(2) —C(11)	119(2)
C(29) —O(3) —C(26)	121(2)	C(30) —O(4) —C(29)	118(2)
C(45) —O(5) —C(48)	114(2)	C(49) —O(6) —C(48)	116(2)
O(2) —C(10) —O(1)	114(2)	O(3) —C(29) —O(4)	114(2)
O(5) —C(48) —O(6)	116(2)		

hedron carbon. This indicates that the methylene bridge C atom has sp^2 bonding geometry, thus the bridge chains (methylenedioxy-bridged bis-iminophenyl moieties) linked to two metals are slightly conjugated (*i.e.*, super-conjugation). It is possible there is a weak metal-metal interaction through the super-conjugated bridges. The cyclic voltammogram of 3 in acetonitrile (Fig. 3) shows a single quasi-reversible oxidation wave centered at +0.24 V *vs.* Ag-AgCl, due to a two-electron Cu(I) / (II) based oxidation process. The result supports the stabilization of the two Cu(I) ions in the trenderived Schiff-base cryptand and there is a weak interaction between the two metal centers. In contrast, a dinuclear copper(I) cryptate of a tren-derived Schiff-base cryptand was reported [23] to display two oxidation waves separated by 220 mV, indicating a strong interaction between the two metal centers. The difference results mainly from the different Cu···Cu separation. In cryptate 3 the Cu···Cu separation is over 12 Å; but in the reported [23] case, that is about 4.4 Å.

The dinuclear copper(I) cryptate 3 is very stable to air and silver(I) ion and it does not show inclusion of 4,4′-bipyridine, imidazole, N_3^-, Na^+, K^+ and NH_4^+. Apparently, this cannot be attributed to its large volume and weak metal-metal interaction. This is possibly due to both the highly effective cryptating about the copper(I) ions and the twisting among the three bridge chains of the cryptand. The O_6 donors do not show affinity toward IA metal ions and NH_4^+, in contrast to most fatty O-containing cryptands [5]. This possibly results from the conjugation of the aromatic oxygen. However, hydrated La^{3+} ion can promote the dissociation of the Schiff-base cryptand into starting polyamine and dialdehyde, as requested by NMR observations. In contrast, a dicopper(I) cryptate of a trpn-derived Schiff-base cryptand has also been reported [24] to behave similarly to 3, although the trpn-derived Schiff-base cryptand has less effective coordination towards the metal ions than that does the tren-derived analogue. In that case, Cu···Cu separation is 4.44(1) Å; therefore, interaction between the two metal centers should be considered beyond the coordination by the four nitrogens.

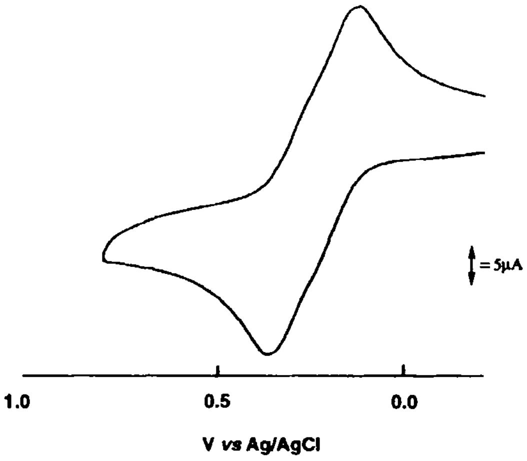

FIGURE 3 Cyclic voltammogram of 3.

Acknowledgments

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Supporting Information Available

Tables of crytallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factor (17 pages).

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