Bull. Chem. Soc. Jpn., **78**, 2161–2163 (2005)

Chiral Distortion of Di(μ-sulfido)-bis[oxomolybdenum(V)] Complexes of a Hexadentate Ligand *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)-*R*-propylenediamine and Its Analogs

Hai-Ying Jin, Ryoichi Hazama, Mikio Yamasaki,[1] Keisuke Umakoshi,*[,2] Kiyoshi Tsuge, and Yoichi Sasaki*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

[1]Rigaku Corporation, Matsubara, Akishima, Tokyo 196-8666

[2]Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852-8521

Received July 11, 2005; E-mail: ysasaki@sci.hokudai.ac.jp

Chiral distortion of the basal four pyridyl nitrogen donors of the titled complex $[Mo_2(O)_2(\mu\text{-}S)_2\{\mu\text{-}N,N,N',N'\text{-tetrakis(2-pyridylmethyl)-}R\text{-propylenediamine}\}]^{2+}$ has been found to be the reverse to that of the corresponding di-μ-oxo complex, on the basis of the inverse pattern of the circular dichroism spectra. Asymmetric distortion of the dimolybdenum(III) dimer $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)\{\mu\text{-}N,N,N',N'\text{-tetrakis(2-pyridylmethyl)ethylenediamine}\}]^{3+}$ has also been discussed.

The molybdenum(V) and tungsten(V) dimers of the hexadentate ligands, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (edta) and its *R*-propylenediamine analog (*R*-pdta), have been prepared[1] for the core structures, $Mo_2O_2(\mu\text{-}O)_2$,[2a,b] $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)$,[2a] $Mo_2O_2(\mu\text{-}S)_2$,[2c] $MoWO_2(\mu\text{-}O)_2$,[2d] $MoWO_2(\mu\text{-}O)(\mu\text{-}S)$,[2e] $W_2O_2(\mu\text{-}O)_2$,[2f,g] $W_2O_2(\mu\text{-}O)(\mu\text{-}S)$,[2h] and $W_2O_2(\mu\text{-}S)_2$.[2i] A molybdenum(III) edta dimer with a $Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)$ core has also been prepared.[2j,k] The hexadentate ligands act as a bridge between the two metal centers with each half of the ligands (bis(carboxymethyl)amino moiety) coordinating to each metal ion of the dimer. X-ray structural analyses revealed that the four basal coordinating atoms (carboxylate oxygen atoms) of the ligand take a non-planar tetrahedrally distorted arrangement. The distortion is associated with the δ- or λ-gauche conformation of the diamine bridge. In the case of the *R*-pdta complexes, the conformation is stereoselectively fixed to λ. For the edta complexes, a pair of enantiomers are found in the crystal. The tetrahedral distortion associated with the λ-conformation is always the Δ configuration as defined in Fig. 1 for all of the edta and *R*-pdta complexes; thus the λ-Δ and δ-Λ relationships hold.[3]

Analogous hexadentate ligands, *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) and the optically active *R*-propylenediamine analog (*R*-tppn) also give similar dimeric complexes for the $Mo^V_2O_2(\mu\text{-}O)_2$ and $W^V_2O_2(\mu\text{-}O)_2$ cores.[1,4] An unusual feature of the structures of these dimers is the reverse stereochemical correlation; Λ configuration for the λ diamine gauche. The exceptional stereochemistry observed for the tpen and *R*-tppn complexes has been considered a result of the steric repulsion between the terminal oxo ligands and the more bulky pyridyl rings.[4]

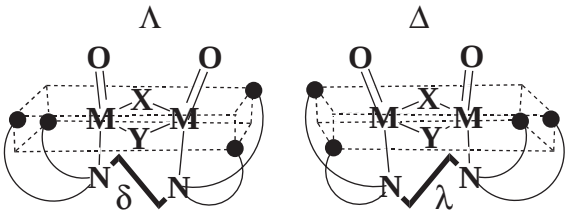

Fig. 1. Correlation between the diamine gauche conformation and the tetrahedral distortion of the four basal donor atoms.

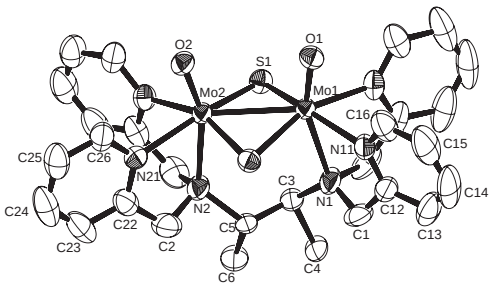

Fig. 2. ORTEP drawing of $[Mo_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})]^{2+}$ with the atomic numbering scheme showing 50% probability thermal ellipsoids. Note that the bridging diamine part is propanediamine, C4 and C6 being disordered independent carbons. C3*, C4*, C5*, and C6* atoms are omitted for clarity.

It has been suggested that the circular dichroism spectrum (CD) in the region >300 nm is useful for diagnosis of the distortion of Mo(V) and W(V) dimers in solution; i.e. the positive maximum and negative maximum for Λ and Δ configurations at around 380–400 nm, respectively.[1,3,4] The CD sign is consistent with the solid-state structure without exceptions and is applicable not only to the complexes of the hexadentate ligands, but also to those with other optically active amino acids.[1,3,4]

We have prepared a similar dimolybdenum(V) complex where the two oxo bridges are replaced with two sulfido ligands. Although we were unable to obtain crystals of good qualiy for the *R*-tppn complex, the complex of the racemic mixture gave crystals of good quality. Figure 2 shows the ORTEP drawing of the complex cation, $[Mo^V_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})]^{2+}$.[5] The Mo–Mo distance is 2.771(1) Å, which is significantly longer than that (2.541(2) Å) of $[Mo^V_2(O)_2(\mu\text{-}O)_2(\mu\text{-}R\text{-tppn})]^{2+}$,[4] but is similar to those of other $Mo^V_2(O)_2(\mu\text{-}S)_2$ complexes.[1,6] The crystal is composed of a disordered mixture of *R*- and *S*-tppn complexes and is analyzed by a model with a mirror plane including two Mo and two terminal O atoms. Crystallographically, there is no asymmetric distortion of the four basal pyridyl nitrogen atoms, although the diamine bridging part is analyzed as a disordered mixture of λ (*R*-tppn

Published on the web December 9, 2005; DOI 10.1246/bcsj.78.2161

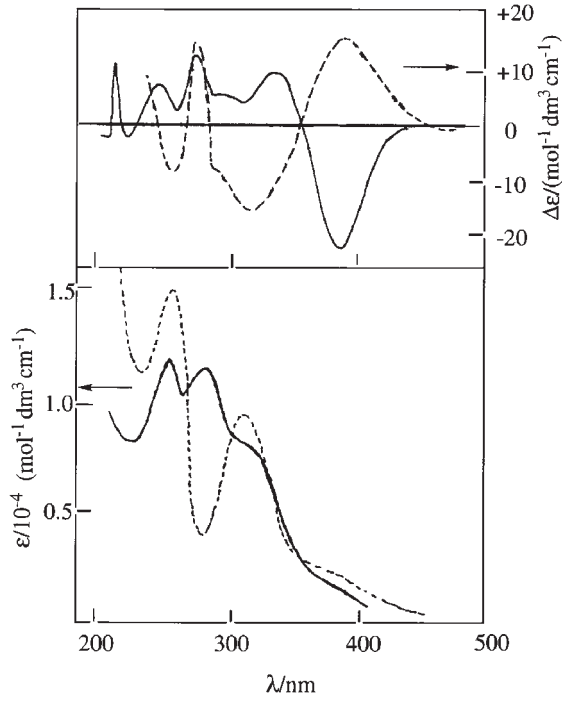

Fig. 3. Electronic absorption (lower) and circular dichroism spectra (upper) of $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R\text{-tppn})]^{2+}$ (solid line) and $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-}R\text{-tppn})]^{2+}$ (broken line) in acetonitrile.

complex) and δ conformations (*S*-tppn complex). Figure 3 shows the electronic absorption and circular dichroism spectra of $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R\text{-tppn})]^{2+}$ and $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-}R\text{-tppn})]^{2+}$ in acetonitrile. Particularly, noteworthy is the almost inversed pattern of the CD spectra in the region >300 nm. While the CD pattern of the di-μ-oxo *R*-tppn complex is consistent with the Λ configuration, that of the di-μ-sulfido complex indicates the Δ configuration. We believe that the asymmetric distortion of the latter is in fact kept in the crystals as judged from previous cases, where the distortions in the crystals and in solution are always consistent. Asymmetric distortion of the di-μ-sulfido complex may be small enough to cause the disorder of the two enantiomeric complex cations in the crystal. It has been concluded that, although crystallographically invisible, the basal plane of the ion $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R\text{-tppn})]^{2+}$ does in fact distort, but clearly in the reverse direction to that of $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-}R\text{-tppn})]^{2+}$, and follows a more commonly observed λ–Δ relationship. The steric repulsion between the oxo ligands and pyridyl rings are now less significant in the di-μ-sulfido complex. Results are summarized in Table S1.

A molybdenum(III) dimer with two hydroxo bridges has also been prepared and its structure examined (Fig. 4).[5] The Mo–Mo distance (2.431(1) Å) and Mo–O(OH^-) are essentially identical to those of the edta complex.[2j,k] Tetrahedral distortion of the new Mo(III) complex follows the more common λ–Δ relationship. It is now clear that the λ–Λ relationship is exceptional and observed only for the more sterically crowded $Mo^{V}_2(O)_2(\mu\text{-}O)_2$ and $W^{V}_2(O)_2(\mu\text{-}O)_2$ complexes.

The cyclic voltammogram of $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R\text{-tppn})]^{2+}$ in acetonitrile shows two quasi-reversible redox

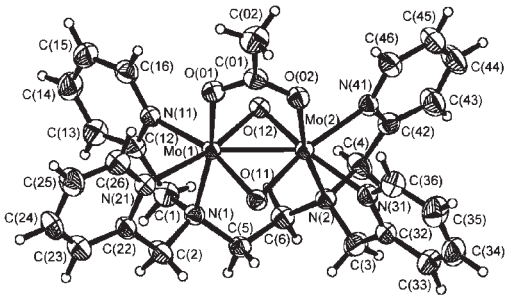

Fig. 4. ORTEP drawing of $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})]^{3+}$ with the atomic numbering scheme showing 50% probability thermal ellipsoids.

waves at −1.14 and −1.81 V vs SCE ($\Delta E = 0.67$ V), which are assigned to the couples Mo_2(V,V)/(V,IV) and Mo_2(V,IV)/(IV,IV), respectively. The comproportionation constant $K_{com} = [Mo_2(IV,V)]^2/\{[Mo_2(V,V)][Mo_2(IV,IV)]\}$ is estimated with ΔE as 2.3×10^{11}. Corresponding waves of the di(μ-O) complex, $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-tpen})]^{2+}$ are observed at −1.89 and −2.35 V, respectively. A shift to the positive potentials as the bridging oxo is replaced by sulfido is the same trend observed for the corresponding edta complexes, $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-edta})]^{2+}$ (−1.89 V, irreversible) and $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-edta})]^{2+}$ (−2.22 V, irreversible), in acetonitrile. The trend is explained by considering that the sulfur d orbitals stabilize $Mo_2(\mu\text{-}S)_2$ molecular orbitals more than oxo bridges do.[7]

Experimental

Preparation of $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R\text{-tppn})](ClO_4)_2\cdot 2H_2O$. A solution of $Na_2[Mo_2(O)_2(\mu\text{-}S)_2(R\text{-cys})_2]\cdot 2H_2O$[8] (0.54 g, 0.84 mmol) in 20 cm^3 of 0.5 M HCl was stirred for 30 min. A methanol solution (5 cm^3) of *R*-tppn (0.36 g, 0.82 mmol) was added to the solution. The pH of the solution was then adjusted to below 4 by adding Na_2CO_3. After filtration, the reddish orange filtrate was diluted with the same amount of water. The solution was then passed through a column of CM-Sephadex C-25 cation exchange regin *in Na^+ form*. The orange band was eluted with 1 M NaCl solution to obtain a yellow eluate, which was evaporated to dryness. The residue was extracted with acetonitrile. The extract was concentrated to obtain a yellow precipitate, which was recrystallized from 15 cm^3 of methanol by adding an excess of $NaClO_4$. The product was collected and dried in vacuo. Yield 0.26 g (33.7%). Anal. Calcd for $C_{27}H_{34}N_6O_{12}Cl_2S_2Mo_2$: C, 33.73; H, 3.70; N, 8.58; S, 6.67; Cl, 7.37%. Found: C, 33.80; H, 3.63; N, 8.94; S, 6.62; Cl, 7.80%. UV–vis (CH_3CN)/nm: 264 (ε, 1.29×10^4 M^{-1} cm^{-1}), 279 (1.13×10^4), 315 (9.14×10^3), 383 (1.99×10^3). IR (KBr disk)/cm^{-1}: 486 (Mo–S), 950 (Mo=O). ^{1}H NMR (CD_3CN)/ppm: δ 9.34–9.26 (m, 4H, pyridyl 6-H), 8.08 (m, 4H, pyridyl 4-H), 7.63 (m, 4H, pyridyl 5-H), 7.53 (m, 4H, pyridyl 3-H), 4.36–3.95 (m, 8H, py–CH_2–), 3.27–2.92 (2H, –CHCH$_3$–CH_2–), 2.49–2.43 (d, 1H, –C*H*CH$_3$–CH$_2$–), 1.19 (d, 3H, –CHCH_3–CH$_2$–). The racemic *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-*R*,*S*-propylenediamine analog was obtained similarly by using racemic ligand instead of *R*-tppn. *Caution*: Perchlorate is potentially explosive and must be treated only in small amount with extreme care.

Preparation of $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})](PF_6)_2(CH_3COO)\cdot 2CH_3COOH\cdot 2H_2O$. The dimolybdenum(V) complex of tpen $[Mo^{V}_2(O)_2(\mu\text{-}O)_2(\mu\text{-}R\text{-tpen})](ClO_4)_2$ (100 mg, 0.13 mmol)[4] was dissolved in 25 cm^3 of aqueous acetate buffer solution (pH, ca. 5). Zinc amalgam (10 g) was added to the solution,

and the mixture was stirred vigorously for 10 min after the introduction of argon gas to remove oxygen. The color of the solution changed to green during the stirring. The mixture was then kept in a refrigerator after addition of $(NH_4)PF_6$ (64 mg, 0.39 mmol). After 3 days, green crystals were deposited, which were used for the X-ray structural analysis. The crystals were heavily contaminated with the original dimolybdenum(V) complex, making them unfit for use in other measurements. Further attempts to obtain pure samples all failed; therefore relevant spectral and cyclic voltammetric measurements were not carried out.

X-ray Structural Analysis. Single crystal X-ray diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å).[5] The crystal structures of $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})](ClO_4)_2 \cdot 4CH_3CN$ and $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})](PF_6)_2(CH_3COO) \cdot 2CH_3COOH \cdot 2H_2O$ were solved by direct method by using SIR2002[9] and SIR92,[10] respectively. The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. Because the methyl group in the propylenediamine moiety is disordered and the crystallographically imposed mirror plane passes through Mo1, Mo2, O1, O2, N1, and N2 atoms, an occupancy factor of 0.5 was assigned to C3 and C5 atoms and that of 0.25 was assigned to C4 and C6 atoms, respectively for $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})](ClO_4)_2 \cdot 4CH_3CN$. All calculations were performed using the CrystalStructure[11] for $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})](ClO_4)_2 \cdot 4CH_3CN$ and teXsan[12] for $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})](PF_6)_2(CH_3COO) \cdot 2CH_3COOH \cdot 2H_2O$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-279689 and -279690 for $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})](ClO_4)_2 \cdot 4CH_3CN$ and $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})](PF_6)_2(CH_3COO) \cdot 2CH_3COOH \cdot 2H_2O$, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Other Measurements. Electronic absorption and circular dichroism spectra were recorded on a HITACHI U-3000 spectrophotometer and JASCO J-720 spectropolarimeter, respectively. ^{1}H NMR spectra were obtained at room temperature at 270 MHz by using a JNM-EX270 spectrometer. Cyclic voltammetry was performed with a BAS CV-50W potentiostat. The working and the counter electrodes were a glassy-carbon disk and a platinum wire, respectively. The reference electrode was Ag/AgCl against which the half-wave potential of Fc/Fc^+ ($E_{1/2}(Fc^{0/+})$ was 0.453 V. The sample solution was prepared in 0.1 M $TBAPF_6$ (tetra(*n*-butyl)ammonium hexafluorophosphate) acetonitrile.

Supporting Information

Table S1 (Asymmetic Distortion Angles of Dinuclear Molybdenum Complexes of Hexadentate Ligands) is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

References

1 K. Saito, Y. Sasaki, and R. Hazama, *J. Cluster Sci.*, **6**, 549 (1995).

2 a) A. Kojima, S. Ooi, Y. Sasaki, K. Z. Suzuki, K. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **54**, 2457 (1981). b) K. Mukerjee, P. Roychowdhury, K. Roy, D. Mukherjee, and M. Kusunoki, *Acta Crystallogr., Sect. C*, **51**, 32 (1995). c) B. Spivack and Z. Dori, *J. Chem. Soc., Dalton Trans.*, **1973**, 1173. d) S. Ikari, Y. Sasaki, A. Nagasawa, C. Kabuto, and T. Ito, *Inorg. Chem.*, **28**, 1248 (1989). e) S. Ikari, Ph.D. Thesis, Tohoku University (1990). f) S. Ikari, Y. Sasaki, and T. Ito, *Inorg. Chem.*, **29**, 53 (1990). g) J. Novak and J. Podlaha, *J. Inorg. Nucl. Chem.*, **36**, 1061 (1974). h) S. Ikari, Y. Sasaki, and T. Ito, *Inorg. Chem.*, **28**, 447 (1989). i) M. Yamazaki and T. Shibahara, *Inorg. Chim. Acta*, **205**, 45 (1993). j) G. G. Kneale, A. J. Geddes, Y. Sasaki, T. Shibahara, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, **1975**, 356. k) G. G. Kneale and A. J. Geddes, *Acta Crystallogr., Sect. B*, **31**, 1233 (1975).

3 K. Z. Suzuki, Y. Sasaki, S. Ooi, and K. Saito, *Bull. Chem. Soc. Jpn.*, **53**, 1288 (1981).

4 R. Hazama, K. Umakoshi, A. Ichimura, S. Ikari, Y. Sasaki, and T. Ito, *Bull. Chem. Soc. Jpn.*, **68**, 456 (1995).

5 Crystal data. $[Mo^{V}_2(O)_2(\mu\text{-}S)_2(\mu\text{-}R,S\text{-tppn})](ClO_4)_2 \cdot 4CH_3CN$: crystal dimensions $0.25 \times 0.25 \times 0.20\,mm^3$, orthorhombic, space group *Pnma*, $a = 20.261(4)$, $b = 15.771(3)$, $c = 13.987(4)$ Å, $V = 4469(2)$ Å^3, $Z = 4$, $T = 293$ K, $\rho_{calcd} = 1.619\,g\,cm^{-3}$, $2\theta_{max} = 55.0^\circ$, $\mu(Mo\,K\alpha) = 8.37\,cm^{-1}$, empirical absorption correction (transmission coefficient: 0.764, 0.846). Reflections: 7575 collected, 5307 unique ($R_{int} = 0.111$), 5307 observed (all data); 320 parameters refined on F^2 with $R = 0.095$ (all data), $wR2 = 0.133$ (all data), GOF = 1.09, residual electron density: +0.56, −0.46 eÅ^{-3}. $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(\mu\text{-tpen})](PF_6)_2(CH_3COO) \cdot 2CH_3COOH \cdot 2H_2O$: crystal dimensions $0.44 \times 0.30 \times 0.20\,mm^3$, monoclinic, space group $P2_1/n$, $a = 10.505(11)$, $b = 19.826(23)$, $c = 22.337(14)$ Å, $V = 4649(6)$ Å^3, $Z = 4$, $T = 298$ K, $\rho_{calcd} = 1.735\,g\,cm^{-3}$, $2\theta_{max} = 50.1^\circ$, $\mu(Mo\,K\alpha) = 7.19\,cm^{-1}$, empirical absorption correction (transmission coefficient: 0.818, 0.866). Reflections: 8950 collected, 8443 unique ($R_{int} = 0.028$), 5549 observed [$I > 2\sigma(I)$]; 573 parameters refined on F with $R = 0.047$ [$I > 2\sigma(I)$], $wR2 = 0.067$ [$I > 2\sigma(I)$], GOF = 1.48, residual electron density: +0.83, −0.91 eÅ^{-3}.

6 T. Shibahara, *Coord. Chem. Rev.*, **123**, 73 (1993).

7 V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977).

8 T. Shibahara, H. Kuroya, H. Akashi, K. Matsumoto, and S. Ooi, *Inorg. Chim. Acta*, **212**, 251 (1993).

9 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, and R. Spagna, SIR2002 (2003).

10 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, and M. Camalli, *J. Appl. Crystallogr.*, **27**, 435 (1994).

11 "CrystalStructure 3.7.0: Crystal Structure Analysis Package," Rigaku and Rigaku/MSC, The Woodlands, TX 77381, USA (2000–2005).

12 "teXsan. Single Crystal Structure Analysis Package," Molecular Structure Corporation, The Woodlands, TX 77381, USA (1992).