Sulfur-Bridged Dinuclear and Tetranuclear Complexes Consisting of *cis*-$[Ru(bpy)_2]^{2+}$ and *cis*-$[Ni(aet)_2]$ Units

Takashi Yoshimura,*[1] **Atsushi Shinohara,**[1] **Masakazu Hirotsu,**[2] **Keiji Ueno,**[3] **and Takumi Konno***[1]

[1]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

[2]Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585

[3]Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515

Received April 27, 2006; E-mail: tyoshi@chem.sci.osaka-u.ac.jp

The 1:1 reaction of $[Ru(bpy)_2(solvent)_2]^{2+}$ (bpy = 2,2′-bipyridine) with $[Ni(aet)_2]$ (aet = 2-aminoethanethiolate) gave a *S*-bridged $Ru^{II}_2Ni^{II}_2$ tetranuclear complex with an eight-membered $Ru_2Ni_2S_4$ metallacycle, $[\{Ru(bpy)_2\}_2\{Ni(aet)_2\}_2]^{4+}$, while a *S*-bridged $Ru^{II}Ni^{II}$ dinuclear complex with a four-membered $RuNiS_2$ metallacycle, $[Ru(bpy)_2\{Ni(aet)_2\}]^{2+}$, was obtained by the corresponding 1:2 reaction between $[Ru(bpy)_2(solvent)_2]^{2+}$ and $[Ni(aet)_2]$.

Coordinated thiolato groups in the square-planar $[M(aet)_2]$ ($M = Ni^{II}$, Pd^{II}; aet = 2-aminoethanethiolate) readily react with transition-metal ions/complexes to form *S*-bridged polynuclear complexes.[1–11] In many cases, the square-planar geometry of $[M(aet)_2]$ is retained in the course of the formation of *S*-bridged polynuclear structures. However, we have found that the square-planar geometry of $[Ni(aet)_2]$ converts to an octahedral geometry during the reaction with $[PtCl_2(bpy)]$ to give a *S*-bridged $Pt^{II}Ni^{II}$ dinuclear complex, $[Pt(bpy)\{Ni(aet)_2(H_2O)_2\}]^{2+}$,[5,6] although the corresponding reaction of $[PtCl_2(bpy)]$ with $[Pd(aet)_2]$ proceeds with retention of the square-planar geometry of $[Pd(aet)_2]$ to afford a *S*-bridged $Pt^{II}_2Pd^{II}_2$ tetranuclear complex, $[\{Pt(bpy)\}_2\{Pd(aet)_2\}_2]^{4+}$.[8] In addition, our recent study has shown that the partial dissociation of aet from $[Pd(aet)_2]$ occurs during the reaction with $[RuCl_2(bpy)_2]$, forming an unique *S*-bridged $Ru^{II}Pd^{II}_3$ tetranuclear complex, $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)_2\}]^{3+}$, in which a $RuPd_2S_3$ metallochelate ring is formed on a $[Ru(bpy)_2]^{2+}$ moiety.[11] Under these circumstances, it is interesting to investigate the *S*-bridged polynuclear structures constructed from $[Ru(bpy)_2]^{2+}$ and $[Ni(aet)_2]$ units. Here, we report that the 1:1 and 1:2 reactions of $[Ru(bpy)_2(solvent)_2]^{2+}$ with $[Ni(aet)_2]$ lead to the formation of different *S*-bridged structures with retention of the square-planar geometry of $[Ni(aet)_2]$.

Treatment of a red solution containing $[Ru(bpy)_2(solvent)_2]^{2+}$ with $[Ni(aet)_2]$ in a 1:1 ratio gave a dark red solution, from which dark red microcrystals **1** were isolated in a reasonable yield by adding an aqueous solution of NH_4PF_6. The elemental analytical data of **1** were in agreement with the formula for a 1:1 adduct of $[Ru(bpy)_2](PF_6)_2$ and $[Ni(aet)_2]$. In the FAB mass spectrum, **1** showed a main signal at $m/z = 1683$, and the calculated molecular mass corresponds to that of the tetranuclear $\{[\{Ru(bpy)_2\}_2\{Ni(aet)_2\}_2](PF_6)_3\}^+$ rather than that for the expected dinuclear $\{[Ru(bpy)_2\{Ni(aet)_2\}](PF_6)\}^+$. The tetranuclear structure for **1** was established by X-ray analysis.

An ORTEP drawing of the complex cation of **1** is shown in Fig. 1. The complex cation of **1** consists of two *cis*-$[Ru(bpy)_2]^{2+}$ and two *cis*-$[Ni(aet)_2]$ units. The two *cis*-$[Ni(aet)_2]$ units adopt a nearly square-planar geometry with Ni atoms being displaced from the N_2S_2 coordination planes only by 0.002 and 0.005 Å. The bond distances and angles about each *cis*-$[Ni(aet)_2]$ unit (av. Ni–S = 2.185(1) Å, Ni–N = 1.949(3) Å, S–Ni–S = 91.50(4)°, N–Ni–N = 90.1(2)°) are within the range observed for *S*-bridged polynuclear complexes containing *cis*-$[Ni(aet)_2]$ units.[3,4,10] In the complex cation of **1**, the two S atoms of each *cis*-$[Ni(aet)_2]$ unit bind with two different *cis*-$[Ru(bpy)_2]^{2+}$ units to form a *S*-bridged $Ru^{II}_2Ni^{II}_2$ tetranuclear structure in $[\{Ru(bpy)_2\}_2\{Ni(aet)_2\}_2]^{4+}$ bearing an eight-membered $Ru_2Ni_2S_4$ metallacycle (Ru⋯Ru = 5.6399(8) Å, av. Ru⋯Ni = 3.9044(7) Å, and Ni⋯Ni = 5.568(1) Å). The coordination geometry of each Ru atom is approximately octahedral, bound by two S atoms from two *cis*-$[Ni(aet)_2]$ units and four N atoms from two bpy ligands (av. *trans* N–Ru–N = 172.6(1)°, *trans* N–Ru–S = 171.7(1)°, S–Ru–S = 89.06(4)°). The Ru–S distances (av. 2.405(1) Å) are slightly longer than those in a related *S*-bridged $Ru^{II}Pd^{II}_2$ complex, $[Ru(bpy)_2\{Pd_2(aet)_3Cl\}]^{2+}$ (av. 2.380(2) Å), in which a *cis*-$[Ru(bpy)_2]^{2+}$ moiety is chelated by a bidentate-*S*,*S* $[Pd_2(aet)_3]^+$ fragment.[11] The Ru–N distances (av. 2.067(2) Å) are similar to those found in *S*-bridged diruthenium(II) complexes containing *cis*-$[Ru(bpy)_2(thiolato)_2]$ units.[12–14] The two *cis*-$[Ru(bpy)_2(S)_2]^{2+}$ moieties in **1** have the same chiral configuration to form a racemic compound consisting of the ΔΔ and ΛΛ isomers; the former is selected in Fig. 1. All of four S atoms have *R* configuration for the ΔΔ isomer and *S* configuration for the ΛΛ isomer. Thus, the complex cation of **1** possesses an idealized D_2 symmetry with two pseudo 2-fold axes coincident with the Ru–Ru and Ni–Ni lines, although the complex cation has no

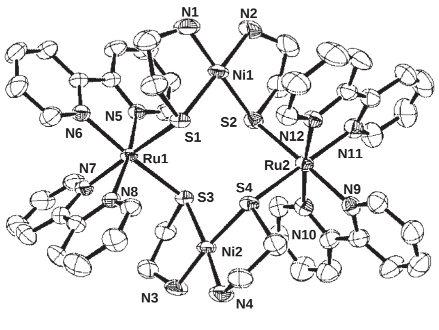

Fig. 1. An ORTEP drawing of the complex cation of **1**. Hydrogen atoms are omitted for clarity.

Published on the web November 9, 2006; doi:10.1246/bcsj.79.1745

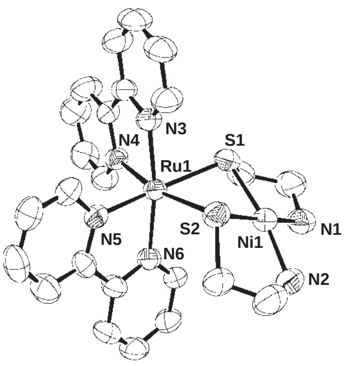

Fig. 2. An ORTEP drawing of the complex cation of **2**. Hydrogen atoms are omitted for clarity.

crystallographically imposed symmetry. In the ^{13}C NMR spectrum in CD_3CN, **1** showed only two methylene carbon signals due to four aet ligands at δ 31.84 and 46.43 and ten aromatic carbon signals due to four bpy ligands in the region of δ 123.51–157.81. This suggests that a racemic ($\Delta\Delta/\Lambda\Lambda$) isomer with a D_2 symmetry is selectively formed for **1**. Based on molecular modeling, the $\Delta\Lambda$ configuration is unfavorable for the $Ru^{II}{}_2Ni^{II}{}_2$ tetranuclear structure in **1**, because of the steric hindrance between the adjacent aet and bpy ligands.

Similar treatment of $[Ru(bpy)_2(solvent)_2]^{2+}$ with $[Ni(aet)_2]$ in a 1:2 ratio also gave a dark red solution, although an appreciable amount of unreacted $[Ni(aet)_2]$ remained. After removal of the unreacted $[Ni(aet)_2]$, dark red crystals **2** were isolated from the filtrate by adding an aqueous solution of NH_4PF_6. The elemental analysis implies that **2** contains $[Ru(bpy)_2](PF_6)_2$ and $[Ni(aet)_2]$ in a 1:1 ratio, as does **1**. Furthermore, the electric absorption spectral features of **2** in CH_3CN are very similar to that of **1** over the whole region, showing intense bands at 481 and 292 nm, which are assigned to a Ru $\rightarrow$ π^*_{bpy} MLCT transition and a $\pi_{bpy} \rightarrow \pi^*_{bpy}$ transition, respectively.[15] From these results, it may be presumed that **2** has a *S*-bridged $Ru^{II}Ni^{II}$ structure similar to that found in **1**. However, the FAB mass spectrum of **2** exhibits a parent peak at $m/z = 769$, which corresponds to the dinuclear $\{[Ru(bpy)_2\{Ni(aet)_2\}](PF_6)\}^+$. The *S*-bridged structure for **2** was also determined by X-ray analysis.

As shown in Fig. 2, the complex cation of **2** contains a *cis*-$[Ni(aet)_2]$ unit that chelates to a *cis*-$[Ru(bpy)_2]^{2+}$ moiety through two S atoms, forming a *S*-bridged $Ru^{II}Ni^{II}$ dinuclear complex with a four-membered $RuNiS_2$ metallacycle, $[Ru(bpy)_2\{Ni(aet)_2\}]^{2+}$ (Ru$\cdots$Ni = 3.194(1) Å). The Ru atom in **2** is situated in an approximately octahedral *cis*-N_4S_2 environment, like the Ru atoms in **1**, and the bond distances and angles around the Ru atom in **2** (av. Ru–N = 2.068(3) Å, av. Ru–S = 2.407(1) Å, *trans* N–Ru–N = 170.8(2)°, *trans* N–Ru–S = 169.1(1)°) are similar to those in **1**. However, the S–Ru–S angle in **2** (76.02(7)°) is much deviated from 90° compared with the S–Ru–S angles in **1** (86.93(5) and 91.18(5)°). Moreover, the *cis*-$[Ni(aet)_2]$ unit in **2** is markedly distorted from a regular square-planar geometry, as indicated by the large displacement of the Ni atom from the N_2S_2 least-square plane (0.118 Å) and the acute S–Ni–S angle (86.58(9)°). Thus, severe distortions around the Ru and Ni atoms as well as around the bridging S atoms (av. Ru–S–Ni = 88.55(6)°) are required for the formation of the four-membered $RuNiS_2$ metallacyclic structure in **2**. As indicated by the space group $P2_1/n$, **2** consists of the Δ and Λ isomers, which combine to form a racemic compound. In contrast to the case for **1**, the chiral configurations of the bridging S atoms are not unified in **2** (Fig. 2), and a racemic pair of the asymmetric ΔSR and ΛRS isomers exists in the crystal. Consistent with this, the ^{13}C NMR spectrum of **2** shows four methylene carbon signals due to two aet ligands (δ 26.44–47.94) and twenty aromatic carbon signals due to two bpy ligands (δ 123.74–158.04), which indicates that the *S*-bridged $Ru^{II}Ni^{II}$ structure in **2** is retained in solution.

In summary, it was found in this study that *cis*-$[Ni(aet)_2]$ functions as a bidentate-*S,S* metalloligand toward *cis*-$[Ru(bpy)_2]^{2+}$. Unlike the reaction of $[Pt(bpy)Cl_2]$ with $[Ni(aet)_2]$, the square-planar Ni^{II} center does not convert to an octahedral geometry, which could be ascribed to the steric crowdness of the *cis*-$[Ru(bpy)_2]^{2+}$ moiety. Remarkably, the *S*-bridged structures constructed from *cis*-$[Ru(bpy)_2]^{2+}$ and *cis*-$[Ni(aet)_2]$ units were found to be affected by the reaction stoichiometries. That is, the *S*-bridged $Ru^{II}{}_2Ni^{II}{}_2$ tetranuclear structure in **1**, where *cis*-$[Ni(aet)_2]$ acts as a bridging metalloligand, was produced from the 1:1 reaction between $[Ru(bpy)_2(solvent)_2]^{2+}$ and $[Ni(aet)_2]$, while the *S*-bridged $Ru^{II}Ni^{II}$ dinuclear structure in **2**, where *cis*-$[Ni(aet)_2]$ serves as a chelating metalloligand, was afforded when excess $[Ni(aet)_2]$ was present in the reaction mixture. X-ray analyses demonstrated that the *S*-bridged structure in **2** with a four-membered $RuNiS_2$ metallacycle is much more distorted than that in **1** with an eight-membered $Ru_2Ni_2S_4$ metallacycle. Thus, we assume that for the 1:1 reaction a $Ru^{II}Ni^{II}$ dinuclear intermediate, in which a *cis*-$[Ni(aet)_2]$ molecule coordinates to a *cis*-$[Ru(bpy)_2]^{2+}$ unit through one S atom, is created at the first stage, followed by its dimerization to form **1**. On the other hand, the presence of excess $[Ni(aet)_2]$ in the reaction mixture would partly generate a $Ru^{II}Ni^{II}{}_2$ trinuclear intermediate, in which two *cis*-$[Ni(aet)_2]$ molecules coordinate to a *cis*-$[Ru(bpy)_2]^{2+}$ unit through one S atom, besides a dinuclear intermediate. This might prevent the dimerization of a $Ru^{II}Ni^{II}$ dinuclear intermediate, leading to the preferential chelation of *cis*-$[Ni(aet)_2]$ to form **2**. Recently, we have shown that the 1:2 reaction of $[Ru(bpy)_2]^{2+}$ with $[Pd(aet)_2]$ gives a *S*-bridged $RuPd_3$ structure in $[Ru(bpy)_2\{Pd_2(aet)_3\}\{Pd(aet)_2\}]^{3+}$ where a *cis*-$[Ru(bpy)_2]^{2+}$ unit is chelated by a bidentate-*S,S* $[Pd_2(aet)_3]^+$ fragment.[11] The formation of this fragment is indicative of the binding of two *cis*-$[Pd(aet)_2]$ molecules to a *cis*-$[Ru(bpy)_2]^{2+}$ unit, accompanied by the dissociation of one aet ligand. It seems that the rigid square-planar geometry of *cis*-$[Pd(aet)_2]$ precludes its chelation to a *cis*-$[Ru(bpy)_2]^{2+}$ unit, and thus, the difference in the flexibility of a square-planar geometry between *cis*-$[Ni(aet)_2]$ and *cis*-$[Pd(aet)_2]$ is responsible for the formation of different *S*-bridged polynuclear structures.

Experimental

Preparation of $[\{Ru(bpy)_2\}_2\{Ni(aet)_2\}_2](PF_6)_4$ (1). To a suspension containing *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$[16] (0.30 g, 0.58 mmol) in acetone (20 mL) was added $AgPF_6$ (0.33 g, 1.30 mmol). The mixture was stirred at room temperature for 2 h under N_2 and was filtered to remove AgCl. To the red filtrate was added $[Ni(aet)_2]$[1] (0.13 g, 0.62 mmol) suspended in water (5 mL) and the mixture was stirred at room temperature for 24 h. To the resulting red solution was added NH_4PF_6 (5.0 g) in water (10 mL), followed by allowing to stand at 4 °C for one day. The red-brown microcrystals **1** deposited were collected by filtration, washed with water, and then dried in air. Yield 0.43 g (79%). Anal. Found: C, 30.79; H, 3.22; N, 8.84%. Calcd for $C_{48}H_{56}F_{24}N_{12}Ni_2P_4Ru_2S_4 \cdot 2H_2O$: C, 30.92; H, 3.24; N, 9.01%. FAB-mass; $m/z = 1683$ for $\{[\{Ru(bpy)_2\}_2\{Ni(aet)_2\}_2](PF_6)_3\}^+$. UV–vis spectrum in CH_3CN [$\lambda_{max/nm}$ (ε/mol^{-1} dm^3 cm^{-1})]: 480 (13600), 347 (13400), 292 (77800), 242 (66200). ^{13}C NMR (CD_3CN; δ from $SiMe_4$): 31.84, 46.43, 123.51, 124.31, 127.04, 127.10, 137.02, 137.31, 150.54, 155.24, 157.70, 157.81. Single crystals of **1** suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its methanol/acetonitrile (1:1) solution.

Preparation of $[Ru(bpy)_2\{Ni(aet)_2\}](PF_6)_2$ (2). To a suspension containing *cis*-$[Ru(bpy)_2Cl_2] \cdot 2H_2O$[16] (0.30 g, 0.58 mmol) in acetone (20 mL) was added $AgPF_6$ (0.33 g, 1.30 mmol). The mixture was stirred at room temperature for 2 h under N_2 and was filtered to remove AgCl. To the filtrate was added $[Ni(aet)_2]$ (0.26 g, 1.24 mmol) suspended in water (5 mL). The mixture was stirred at room temperature for 24 h and was filtered to remove unreacted $[Ni(aet)_2]$ (ca. 0.05 g). To the resulting red solution was added NH_4PF_6 (5.0 g) in water (10 mL), followed by allowing to stand at 4 °C for one day. The red-brown microcrystals **2** deposited were collected by filtration, washed with water, and then dried in air. Yield 0.40 g (75%). Anal. Found: C, 31.24; H, 3.34; N, 8.99%. Anal. Calcd for $C_{24}H_{28}F_{12}N_6NiP_2RuS_2$: C, 31.53; H, 3.09; N, 9.19%. FAB-mass: $m/z = 769$ for $\{[Ru(bpy)_2\{Ni(aet)_2\}](PF_6)\}^+$. UV–vis spectrum in CH_3CN [$\lambda_{max/nm}$ (ε/mol^{-1} dm^3 cm^{-1})]: 481 (7200), 345 (7500), 292 (49200), 243 (33000). ^{13}C NMR (CD_3CN; δ from $SiMe_4$): δ 26.44, 29.14, 46.76, 47.94, 123.74, 126.38, 124.11, 126.38, 126.45, 129.17, 135.91, 136.57, 136.97, 137.89, 151.46, 151.52, 151.96, 155.60, 157.23, 157.56, 158.04. Single crystals of **2** suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its methanol solution.

Measurements. UV–vis absorption spectra were recorded with a JASCO Ubest-55 or V-530 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a JNM-JEOL 300 MHz spectrometer at probe temperature.

X-ray Structure Determinations. Single-crystal X-ray diffraction experiment for $\mathbf{1} \cdot CH_3OH \cdot CH_3CN \cdot 1.5(C_2H_5)_2O$ was performed on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Single-crystal X-ray diffraction experiment for $\mathbf{2} \cdot CH_3OH$ was performed on a Rigaku AFC-7S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell parameters were determined by a least-squares refinement, using the setting angles of 22 reflections in the ranges of $20.24° < 2\theta < 23.48°$. The positions of metal atoms were determined by Patterson methods (DIRDIF94)[17] for $\mathbf{1} \cdot CH_3OH \cdot CH_3CN \cdot 1.5(C_2H_5)_2O$ and direct methods (SIR92)[18] for $\mathbf{2} \cdot CH_3OH$, respectively, and those of the other non-H atoms were determined by difference Fourier techniques. The non-H atoms in the complexes were refined by full-matrix least-squares techniques using anisotropic thermal parameters. The C–C, C–O, and C≡N distances of solvent molecules in $\mathbf{1} \cdot CH_3OH \cdot CH_3CN \cdot 1.5(C_2H_5)_2O$ were fixed at 1.52 Å for C–C and C–O and at 1.20 Å for C≡N, respectively, and refined isotropically. H atoms, except for those of solvent molecules, were placed at calculated positions and refined. All calculations were performed using the teXsan crystallographic software package.[19] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-604923 and -604924. 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).

The authors are grateful to Prof. M. Unno and Prof. H. Matsumoto (Gunma University) for the measurement of X-ray data.

References

1 D. C. Jicha, D. H. Busch, *Inorg. Chem.* **1962**, *1*, 872.

2 D. C. Jicha, D. H. Busch, *Inorg. Chem.* **1962**, *1*, 878.

3 C. H. Wei, L. F. Dahl, *Inorg. Chem.* **1970**, *9*, 1878.

4 T. Konno, K. Yonenobu, J. Hidaka, K. Okamoto, *Inorg. Chem.* **1994**, *33*, 861.

5 T. Konno, Y. Yoshinari, K. Okamoto, *Chem. Lett.* **1995**, 989.

6 K. Okamoto, Y. Yoshinari, Y. Yamada, N. Sakagami, T. Konno, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1363.

7 Y. Yamada, K. Fujisawa, K. Okamoto, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2067.

8 Y. Yamada, K. Fujisawa, K. Okamoto, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2297.

9 H.-W. Xu, Z.-N. Chen, S. Ishizaka, N. Kitamura, J.-G. Wu, *Chem. Commun.* **2002**, 1934.

10 T. Konno, M. Usami, A. Toyota, M. Hirotsu, T. Kawamoto, *Chem. Lett.* **2005**, *34*, 1146.

11 T. Yoshimura, A. Shinohara, M. Hirotsu, T. Konno, *Chem. Lett.* **2005**, *34*, 1310.

12 M. A. Greaney, C. L. Coyle, M. A. Harmer, A. Jordan, E. I. Stiefel, *Inorg. Chem.* **1989**, *28*, 912.

13 N. Matsuura, A. I.-Kamiyama, T. Kawamoto, T. Konno, *Chem. Lett.* **2005**, *34*, 1252.

14 N. Matsuura, T. Kawamoto, T. Konno, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 297.

15 A. Julis, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85.

16 P. A. Lay, A. M. Sargeson, H. Taube, *Inorg. Synth.* **1986**, *24*, 291.

17 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *Technical Report of the Crystallography Laboratory*, University of Nijmegan, **1994**.

18 SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

19 teXsan: *Single Crystal Analysis Software*, Molecular Structure Corporation, **1995**.