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Rare-Earth Nitroquinolinates: Visible-Light-Sensitizable Near-Infrared Emitters in Aqueous Solution

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Water-soluble, stable, and easily synthesizable 1:4 complexes of rare-earth ions with 8-hydroxy-5-nitroquinolinate ligands have been prepared. These complexes can be sensitized by visible light with wavelengths up to 480 nm and show near-infrared emission in aqueous solution. The incorporation of a nitro group in the quinoline moiety shifts its absorption bands to longer wavelengths and also increases its molar absorptivity by a factor of 2.5, thereby significantly enhancing its light-harvesting power. The presence of the nitro group also increases the solubility of the resulting complexes, making them water-soluble.

Introduction

Research towards efficient near-infrared emitting lanthanide systems that are compatible with aqueous media is becoming increasingly popular.[1–6] There are several reasons for this. First of all, in vivo imaging using near-infrared radiation has the advantage of being noninvasive and tissue-friendly because of the longer emission wavelengths used. Secondly, although several rare-earth complexes have been reported to show bright near-infrared emission, most of these systems are soluble in (deuterated) organic solvents only. Moreover, because of the small energy gap between the excited states of the near-infrared emitting lanthanide ion and its lower lying energy levels, the introduction of water into these systems provides a very efficient route for radiationless deactivation, which quenches the luminescence and makes these systems useless for applications.

Lanthanide complexes that exhibit visible emission should preferentially have antenna ligands with triplet levels at rather high energy in order to prevent energy back-transfer from the accepting energy level of the lanthanide ion to the triplet level of the ligand. This usually means that the excitation wavelength of such systems is located in the ultraviolet spectral region, although some visible-light-sensitizable systems have been reported.[7–11] In the case of biosensing applications, it is obvious that excitation with visible light offers the advantage of being less harmful towards living tissue. In lanthanide complexes that emit in the near-infrared, the position of the triplet level can be much lower because of the lower lying emission levels of the lanthanide ion. However, in many cases, excitation of these systems still requires ultraviolet radiation.

Here, we report the visible light sensitization of lanthanide complexes with nitrated 8-hydroxyquinoline ligands. The ligand 8-hydroxy-5-nitroquinoline (Figure 1) forms water-soluble 4:1 complexes with trivalent lanthanide ions that show visible-light-sensitized near-infrared emission in aqueous media. In addition, these complexes can be made in an easy one-step synthetic method.

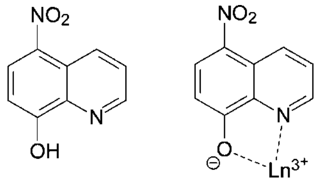

Figure 1. Chemical structure of 8-hydroxy-5-nitroquinoline (left) and its coordination mode to a rare-earth ion (right).

Results and Discussion

8-Hydroxyquinoline has historically been used as a gravimetric agent for the determination of a large variety of metal ions, so its application was mainly based on its good complexing properties and on the low solubility of the resulting complexes in aqueous media.[12] Recently, we have shown that complexes of 8-hydroxyquinoline and its derivatives with trivalent rare-earth ions possess a rich structural chemistry that results in the formation of hydrated 3:1 tris structures, 4:1 tetrakis structures, and 8:3 trimeric species.[13] Because of the promising near-infrared luminescence properties of the quinolinates of trivalent erbium, ytterbium, and neodymium, interest in these materials has in-

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creased substantially in the last years, resulting in the appearance of several literature reports.[14–20]

This paper is the first, however, to report on complexes of 8-hydroxy-5-nitroquinoline as near-infrared emitting materials. Introduction of the nitro group in the 5-position of the 8-hydroxyquinoline moiety changes its physical and chemical properties significantly. The resulting complex is soluble in water at ambient temperature, whereas the non-nitrated equivalents are not. The electron-withdrawing properties of the nitro group decrease the basicity of the coordinating oxygen atom, resulting in the preferential formation of 4:1 tetrakis complexes rather than 8:3 trimeric oxygen-bridged species (an electron-poor oxygen atom is less capable of bridging two rare-earth ions, which is needed to form 8:3 trimeric species). Also, the use of excess ligand and of excess cations in the synthetic procedure stimulates the formation of 4:1 tetrakis complexes instead of 8:3 trimers even though no substituents are present in the 7-position of the quinoline ligand (see Experimental Section). The molecular structure of the yttrium(III) complex of 8-hydroxy-5-nitroquinoline with a tetraethylammonium counterion is shown in Figure 2; the crystal structure data are summarized in the Experimental Section.

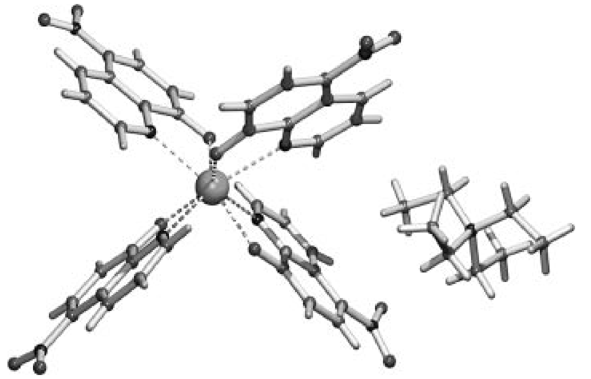

Figure 2. Detail of the molecular structure of the yttrium(III) complex of 8-hydroxy-5-nitroquinoline with a tetraethylammonium counterion.

The structure contains only one tetrakis(nitroquinolinate) complex in the asymmetric unit, together with one tetraethylammonium counter cation. The yttrium(III) ion is surrounded by four nitroquinolinate ligands. The coordination number of the yttrium(III) ion is eight, and the coordination polyhedron can be described as a slightly distorted square antiprism. No solvent molecules are coordinated to the yttrium(III) ion.

Because of the more pronounced electron delocalization in the nitro group, the electronic absorption spectrum of the ligand also differs from that of the non-nitrated equivalents. The absorption spectrum of a nitrated rare-earth quinolinate is shown in Figure 3 along with the luminescence spectra of aqueous solutions of the neodymium(III) and ytterbium(III) complexes of 8-hydroxy-5-nitroquinoline with a tetraethylammonium counterion. The absorption spectrum shows the typical features of deprotonated 8-hydroxyquinolines, namely two absorption bands corresponding to $\pi \rightarrow \pi^*$ transitions. The longer wavelength transition is associated with a shift of electron density from the phenolate oxygen to the π^* orbitals of the aromatic ring.[21] It can easily be seen that the longer wavelength transition allows excitation with visible light with wavelengths of up to 480 nm. Another important effect of the incorporation of the nitro substituent is a significant increase in the molar absorptivity of the complex, which results in an enhanced light harvesting power: the ε value of the neodymium(III) complex of 8-hydroxy-5-nitroquinoline with a tetraethylammonium counterion, measured at the absorption maximum (445 nm), is 36800 $\text{M}^{-1}\,\text{cm}^{-1}$, whereas the ε value of the comparable neodymium(III) complex of 5,7-dichloro-8-hydroxyquinoline with a tetraethylammonium counterion measured at the absorption maximum (405 nm) is only 14300 $\text{M}^{-1}\,\text{cm}^{-1}$.[22]

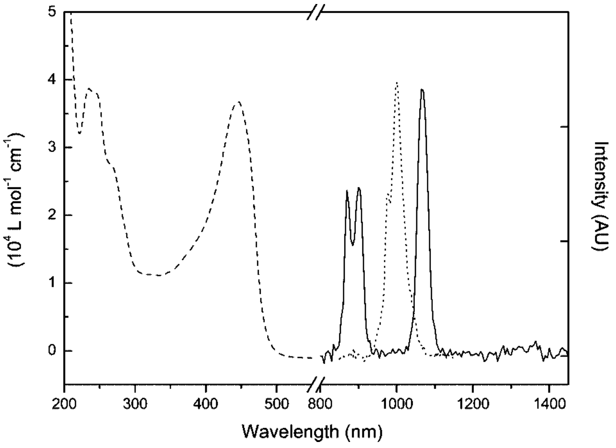

Figure 3. Absorption (dashed line) and emission spectra of the neodymium (solid line) and the ytterbium complexes (dotted line) of 8-hydroxy-5-nitroquinoline with tetraethylammonium counterions in water ($c \approx 10^{-5}$ M; λ_{exc} = 445 nm).

The luminescence spectrum of the neodymium(III) complex shows the typical bands of the ion, two of which are very distinct (${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ at 902 nm and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ at 1067 nm), whereas the ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition can be observed at about 1350 nm, albeit very weak, because of the strong light absorption by water in that spectral region. The luminescence spectrum of the ytterbium(III) complex shows only one band, corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, centered at 1001 nm. The concentrations of the solutions were between 10^{-6} and 10^{-5} M. An overview of the luminescence decay times, τ, and the calculated level quantum efficiencies, Φ, of the neodymium(III) and ytterbium(III) complexes of 8-hydroxy-5-nitroquinoline, both in water and in thf, is given in Table 1. Because of the difficulties involved in performing reliable quantum yield measurements, we decided not to measure these values but to calculate approximate values by comparing the luminescence decay time, τ, with the radiative lifetime, τ_0, of the ions, taken from the literature: $\Phi = \tau/\tau_0 \times 100\,\%$. The radiative lifetime, τ_0, of Nd^{3+} was taken to be 0.25 ms, whereas that of Yb^{3+} is 2 ms.[23]

Table 1. Luminescence decay times, τ, of the Nd^{3+} ($^4F_{3/2}$) and Yb^{3+} ($^2F_{5/2}$) levels and calculated level quantum efficiencies Φ.[a]

Ln^{3+}	Solvent	τ [μs]	Φ [%]
Nd^{3+}	thf	0.51	0.20
	water	0.47	0.19
Yb^{3+}	thf	8.3	0.41
	water	1.4	0.07

[a] Lifetimes measured at room temperature; λ_{exc} = 355 nm; $c \approx 10^{-5}$ M.

The luminescence decay times of the neodymium(III) and ytterbium(III) complexes in thf (Table 2) are typical for complexes of these ions in an organic solvent.[24] In water, two striking features become obvious: 1) there is hardly any difference in the efficiency of the neodymium(III) complex in water as compared to thf, and 2) the efficiency of the ytterbium(III) complex in water is much lower than in thf. The first feature can be explained by looking at the crystal structure (Figure 2), from which it is obvious that no solvent molecules are coordinated to the central metal ion. It seems that the four ligands form a very efficient shell around the lanthanide ion.[25,26] These values compare well with those found by Imbert et al.[5] and Comby et al.,[6] who reported luminescence decay times for neodymium(III) complexes of a hydroxyquinoline-containing podand in water of between 0.13 and 0.25 μs. In these reports, however, the efficiencies of the ytterbium(III) complexes are much better than those of the neodymium(III) complexes, which is in line with what one would expect. A possible explanation for the aberrant behavior of the ytterbium(III) complex in our system could be the nitro substituent on the quinoline moiety, although the difference in redox potentials between the neodymium(III) and ytterbium(III) ions is also known to have an influence.[27] We are currently investigating the energy-transfer properties of these nitroquinolinate complexes in more detail.

Conclusions

In conclusion, we have shown that visible-light-sensitizable near-infrared emission can be obtained from neodymium(III) and ytterbium(III) complexes of 8-hydroxy-5-nitroquinoline in aqueous solution. This is the first report in which this nitrated quinoline has been used as a ligand for near-infrared-emitting lanthanide ions. The incorporation of a nitro group in the quinoline moiety shifts its absorption bands to longer wavelengths and also increases its molar absorptivity by a factor of 2.5, thereby significantly enhancing its light-harvesting power. Furthermore, the resulting 4:1 complexes are water-soluble.

Experimental Section

Equipment and Techniques: Absorption spectra were recorded with a Varian Cary 5000 spectrophotometer. The steady-state near-infrared luminescence spectra and the decay time measurements were recorded on an Edinburgh Instruments FS920P near infrared spectrometer, with a 450-W xenon lamp as the steady-state excitation source, a double excitation monochromator with 1800 lines per millimeter, an emission monochromator with 600 lines per millimeter, and a liquid-nitrogen-cooled Hamamatsu R5509-72 near-infrared photomultiplier tube. For luminescence decay time measurements, the setup includes a Continuum Minilite Nd:YAG laser, equipped with 2nd, 3rd and 4th harmonic crystals, which allows excitation at 1064, 532, 355, and 266 nm. Repetition rate: 10 Hz; pulse width: 3–5 ns. Standard quartz 1-cm fluorescence cuvettes (Hellma type QS-111) were used. CHN elemental analyses were performed with a CE Instruments EA-1110 elemental analyzer.

Synthesis: 8-Hydroxy-5-nitroquinoline was purchased from Acros. Sodium hydroxide, sodium chloride, tetraethylammonium hydroxide, tetraethylammonium chloride, yttrium(III) chloride hexahydrate, neodymium(III) chloride hexahydrate, and ytterbium(III) chloride hexahydrate were purchased from Aldrich.

$NEt_4[Y(Q5N)_4]\cdot 2H_2O$ (HQ5N = 8-hydroxy-5-nitroquinoline): In a first step, 0.75 mmol of 8-hydroxy-5-nitroquinoline was added to 50 mL of water together with 0.75 mmol of tetraethylammonium hydroxide solution and 3 mmol of tetraethylammonium chloride (to have a large excess of the counterion). The solution was then heated to 60 °C until the ligand had completely dissolved. The pH was checked and, if lower than 7.5, some extra hydroxide base was added. Subsequently, 0.15 mmol of yttrium(III) chloride hexahydrate in 10 mL of water was slowly added and the resulting solution was stirred for an hour. After cooling, the water was removed by evaporation under reduced pressure. The resulting oily product was dissolved in a small amount of methanol (approx. 5 mL). The precipitate formed was washed with small amounts of water and ethanol. Yield: 64 mg (34%). $C_{44}H_{40}N_9O_{12}Y\cdot 2H_2O$ (1011.8): calcd. C 52.23, H 4.38, N 12.46; found C 52.49, H 4.31, N 12.14. ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.15 [t, 3 H, $N(CH_2CH_3)_4$], 3.17 [q, 2 H, $N(CH_2CH_3)_4$], 6.62 (d, 1 H, H^7), 7.74 (dd, 1 H, H^3), 8.46 (d, 1 H, H^4), 8.96 (d, 1 H, H^6), 9.26 (d, 1 H, H^2) ppm. MS (ESI$^-$): *m/z* 845 $[Y(Q5N)_4]^-$.

$Na[Nd(Q5N)_4]\cdot H_2O$: In a first step, 0.75 mmol of 8-hydroxy-5-nitroquinoline was added to 50 mL of water together with 0.75 mmol of sodium hydroxide solution and 3 mmol of sodium chloride (to have a large excess of the counterion). The solution was then heated to 60 °C until the ligand had completely dissolved. The pH was checked and, if lower than 7.5, some extra hydroxide base was added. Subsequently, 0.15 mmol of neodymium(III) chloride hexahydrate in 10 mL of water was slowly added and the resulting solution was stirred for an hour. After cooling, a precipitate formed, which was filtered off and washed with small amounts of water and ethanol. Yield: 102 mg (58%). $C_{36}H_{20}N_8NaNdO_{12}\cdot H_2O$ (941.84): calcd. C 45.91, H 2.35, N 11.90; found C 46.12, H 2.29, N 11.78. The solubility in EtOH/chloroform was too low to obtain good mass spectra.

$NEt_4[Yb(Q5N)_4]\cdot 3H_2O$: In a first step, 0.75 mmol of 8-hydroxy-5-nitroquinoline was added to 50 mL of water together with 0.75 mmol of tetraethylammonium hydroxide solution and 3 mmol of tetraethylammonium chloride (to have a large excess of the counterion). The solution was then heated to 60 °C until the ligand had completely dissolved. The pH was checked and, if lower than 7.5, some extra hydroxide base was added. Subsequently, 0.15 mmol of ytterbium(III) chloride hexahydrate in 10 mL of water was slowly added and the resulting solution was stirred for an hour. After cooling, the water was removed by evaporation under reduced pressure. The resulting oily product was dissolved in a small amount of methanol (approx. 5 mL). The precipitate formed was washed with small amounts of water and ethanol. Yield: 84 mg

(40%). $C_{44}H_{40}N_9O_{12}Yb\cdot3H_2O$ (1113.9): calcd. C 47.44, H 4.16, N 11.32; found C 47.58, H 4.01, N 11.22. MS (ESI$^-$): m/z 930 $[Yb(Q5N)_4]^-$.

Crystal Data for the Yttrium(III) Complex of 8-Hydroxy-5-nitroquinoline: Crystals were obtained by diffusion of diethyl ether into a solution of the compound in dmf. Intensity data were collected on a SMART 6000 diffractometer equipped with a CCD detector using Cu-K_α radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker.[28] $[C_8H_{20}N][C_{36}H_{20}N_8O_{12}Y]$, M = 975.76, monoclinic, $P2_1/c$, a = 17.771(2), b = 13.994(1), c = 16.893(2) Å, β = 96.063(6)°, V = 4177.7(8) Å^3, T = 100 K, Z = 4, D_c = 1.551 g cm^{-3}, μ(Cu-K_α) = 2.632 mm^{-1}, F(000) = 2008, crystal size 0.3 × 0.3 × 0.1 mm^3, 7338 independent reflections (R_{int} = 0.1359). Final R = 0.0918 for 3940 reflections with $I > 2\sigma(I)$ and ωR_2 = 0.2488 for all data. See Table 2 for further details. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[29] Non-hydrogen atoms were refined anisotropically and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2-times U(eq) of the parent atoms (1.5-times for methyl groups). The refinement of the data was difficult due to the low diffraction intensity at higher 2θ angles.

Table 2. Summary of crystal data, intensity measurements, and structure refinement of the yttrium complex.

Formula	$C_{44}H_{40}N_9O_{12}Y$
Molecular weight	975.76
Crystal dimensions [mm]	0.3 × 0.3 × 0.1
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	17.771(2)
b [Å]	13.994(1)
c [Å]	16.893(2)
α [°]	90
β [°]	96.063(6)
γ [°]	90
V [Å^3]	4177.7(8)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.551
μ(Cu-K_α) [mm^{-1}]	2.632
Absorption correction	refined from ΔF
F(000)	2008
Measured reflections	8236
Unique reflections	7338
Observed reflections [$I_o > 2\sigma(I_o)$]	3940
Parameters refined	599
Goodness-of-fit	1.015
R_1	0.0918
ωR_2	0.2129
R_1 (all data)	0.1719
ωR_2 (all data)	0.2488

CCDC-619338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] M. H. V. Werts, R. H. Woudenberg, P. G. Emmerink, R. van Gassel, J. W. Hofstraat, J. W. Verhoeven, *Angew. Chem. Int. Ed.* **2000**, *39*, 4542–4544.
[2] J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048–1077.
[3] Y. Korovin, N. Rusakova, *Inorg. Chem. Rev.* **2001**, *21*, 299–329.
[4] J.-C. G. Bünzli, G. R. Choppin, in *Lanthanide Probes in Life, Chemical and Earth Sciences – Theory and Practice*, **1989**, Elsevier, Amsterdam.
[5] D. Imbert, S. Comby, A.-S. Chauvin, J.-C. G. Bünzli, *Chem. Commun.* **2005**, 1432–1434.
[6] S. Comby, D. Imbert, A.-S. Chauvin, J.-C. G. Bünzli, *Inorg. Chem.* **2006**, *45*, 732–743.
[7] M. H. V. Werts, M. A. Duin, J. W. Hofstraat, J. W. Verhoeven, *Chem. Commun.* **1999**, 799–800.
[8] R. Van Deun, P. Nockemann, P. Fias, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Chem. Commun.* **2005**, 590–592.
[9] N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. D. Ward, *Chem. Commun.* **2003**, 1134–1135.
[10] J.-M. Herrera, S. J. A. Pope, H. Adams, S. Faulkner, M. D. Ward, *Inorg. Chem.* **2006**, *45*, 3895–3904.
[11] D. Imbert, M. Cantuel, J.-C. G. Bunzli, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2003**, *125*, 15698–15699.
[12] E. R. Birnbaum, J. H. Forsberg, *Gmelin Handbook of Inorganic Chemistry, Sc, Y, La–Lu Rare Earth Elements*, Springer-Verlag, Berlin, **1982**; Part D2, System Nr. 39, p. 5–24 and references cited therein.
[13] R. Van Deun, P. Fias, P. Nockemann, A. Schepers, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Inorg. Chem.* **2004**, *43*, 8461–8469.
[14] M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1359–1363.
[15] W. P. Gillin, R. J. Curry, *Appl. Phys. Lett.* **1999**, *74*, 798–799.
[16] S. W. Magennis, A. J. Ferguson, T. Bryden, T. S. Jones, A. Beeby, I. D. W. Samuel, *Synth. Met.* **2003**, *138*, 463–469.
[17] J. Thompson, R. I. R. Blyth, G. Gigli, R. Cingolani, *Adv. Funct. Mater.* **2004**, *14*, 979–984.
[18] F. Artizzu, P. Deplano, L. Marchio, M. L. Mercuri, L. Pilia, A. Serpe, F. Quochi, R. Orru, F. Cordella, F. Meinardi, R. Tubino, A. Mura, G. Bongiovanni, *Inorg. Chem.* **2005**, *44*, 840–842.
[19] F. Quochi, R. Orru, F. Cordella, A. Mura, G. Bongiovanni, F. Artizzu, P. Deplano, M. L. Mercuri, L. Pilia, A. Serpe, *J. Appl. Phys.* **2006**, *99*, 053520.
[20] S. G. Leary, G. B. Deacon, P. C. Junk, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2647–2650.
[21] H. Kunkely, A. Vogler, *Inorg. Chem. Commun.* **2000**, *3*, 645–647.
[22] P. Fias, PhD Thesis, K. U. Leuven, **2005**.
[23] S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. van Veggel, D. N. Reinhoudt, L. H. Slooff, A. Polman, J. W. Hofstraat, *J. Appl. Phys.* **1999**, *86*, 1181–1185.
[24] G. A. Hebbink, L. Grave, L. A. Woldering, D. N. Reinhoudt, F. C. J. M. van Veggel, *J. Phys. Chem. A* **2003**, *107*, 2483–2491.
[25] S. W. Magennis, S. Parsons, Z. Pikramenou, *Chem. Eur. J.* **2002**, *8*, 5761–5771.
[26] A. P. Bassett, R. Van Deun, P. Nockemann, P. B. Glover, B. M. Kariuki, K. Van Hecke, L. Van Meervelt, Z. Pikramenou, *Inorg. Chem.* **2005**, *44*, 6140–6142.
[27] W. D. Horrocks, J. P. Bolender, W. D. Smith, R. M. Supkowski, *J. Am. Chem. Soc.* **1997**, *119*, 5972–5973.
[28] SAINT, Manual Version 5/6.0, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, **1997**.
[29] SHELXTL-PC, Manual Version 5.1, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, **1997**.

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