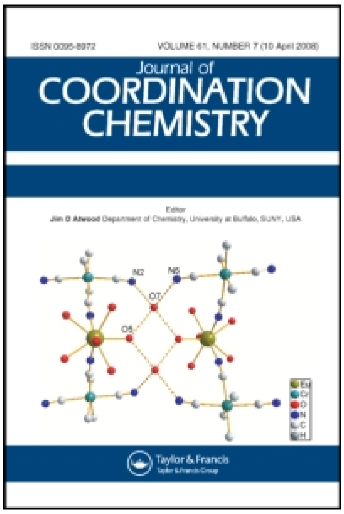


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal structures and nitrosation reactions of triazido complexes of chromium(III)

Anders Kadziola[a]; Anders DØssing[a]
[a] Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

To cite this Article Kadziola, Anders and DØssing, Anders(2008) 'Crystal structures and nitrosation reactions of triazido complexes of chromium(III)', Journal of Coordination Chemistry, 61: 11, 1671 — 1677

To link to this Article: DOI: 10.1080/00958970701617793

URL: http://dx.doi.org/10.1080/00958970701617793

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1671–1677

Taylor & Francis
Taylor & Francis Group

Crystal structures and nitrosation reactions of triazido complexes of chromium(III)

ANDERS KADZIOLA and ANDERS DØSSING*

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

(*Received 24 April 2007; in final form 31 May 2007*)

Two triazido chromium(III) complexes $[Cr(tame)(N_3)_3] \cdot H_2O$ (**1**) and $[Cr(tacn)(N_3)_3]$ (**2**) (tame = 1,1,1-tris(aminomethyl)ethane and tacn = 1,4,7-triazacyclononane) have been prepared and characterized by single-crystal X-ray crystallography at 122 K. The crystal structure of **1** is monoclinic, space group $P2_1/c$, with $a = 9.2460(9)$, $b = 11.0500(11)$, $c = 13.1980(9)$ Å, $\beta = 97.244(7)^\circ$ with four formula units in the cell. The crystal structure of **2** is triclinic, space group $P\bar{1}$, with $a = 7.698(4)$, $b = 8.5800(6)$, $c = 10.236(3)$ Å, $\alpha = 89.497(15)$, $\beta = 83.70(2)$, $\gamma = 72.83(2)^\circ$ with two formula units in the cell. The reactions between $NOBF_4$ and **1** or **2** in acetonitrile give $[Cr(tame)(NCCH_3)_3](BF_4)_3$ and $[Cr(tacn)(NCCH_3)_3](BF_4)_3$, respectively.

Keywords: Triazido complexes; Chromium(III); Nitrosation; Crystal structure; Photolysis

1. Introduction

The chemistry of azidochromium(III) complexes has attracted renewed attention since it was discovered that dinitrogen could be released from a chromium(III) azido complex on photolysis, with formation of a chromium(V) nitrido complex [1]. Since then a rich $[Cr^VN]^{2+}$ chemistry has emerged with special focus on the optical properties of the complexes. Moreover, having a d^1 configuration, the electronic structure of the complexes has been investigated by use of EPR spectroscopy [2, 3]. Another characteristic reaction of a coordinated azide ligand is nitrosation. This reaction can be accomplished by use of HNO_2 or the nitrosonium ion, NO^+, in which N_2O and N_2 are formed [4–8]. To study such reactions further, we have synthesized $[Cr(tame)(N_3)_3] \cdot H_2O$ (**1**) and $[Cr(tacn)(N_3)_3]$ (**2**) (tame = 1,1,1-tris(aminomethyl)ethane and tacn = 1,4,7-triazacyclononane). We report here the structures and nitrosation reactions of **1** and **2**.

---

*Corresponding author. Email: dossing@kiku.dk

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701617793

2. Experimental

2.1. *Synthesis*

All chemicals were of reagent grade or better quality. The complexes were subjected to Cr, C, H and N microanalysis. The compounds [Cr(tame)Cl_3] and [Cr(tacn)$(OH_2)_3$]$(CF_3SO_3)_3$ were prepared according to literature procedures [9, 10].

Warning: Azido complexes are potential hazards. They should be prepared in small quantities and protected from heat and shock.

2.1.1. [Cr(tame)$(N_3)_3$] · H_2O (1). 3.66 g (13.3 mmol) of [Cr(tame)Cl_3] was dissolved in 10 cm^3 of triflic acid (CF_3SO_3H). The solution was stirred at 60°C for 2 h during which a pink precipitate formed. After cooling, the precipitate was filtered off, washed with diethyl ether and dried in air. Yield: 7.3 g of [Cr(tame)$(CF_3SO_3)_3$] (90%). This product was used directly in further syntheses: 2.0 g (3.2 mmol) of [Cr(tame)$(CF_3SO_3)_3$] was dissolved in a mixture of 50 cm^3 acetone and 0.3 cm^3 CF_3SO_3H (1 M). The solution was filtered and the filtrate was left for slow evaporation, during which a red precipitate of [Cr(tame)$(OH_2)_3$]$(CF_3SO_3)_3$ formed. This was washed with diethyl ether and dried in air. Yield: 2.0 g (92%). This product was used directly in further syntheses: 0.20 g (0.30 mmol) of [Cr(tame)$(OH_2)_3$]$(CF_3SO_3)_3$ and 0.20 g (3.1 mmol) of NaN_3 were dissolved in 2 cm^3 of water. The resulting violet solution was left overnight for crystallization. The red-violet crystals were washed with water and ethanol and then dried in air. Yield: 80 mg (90%) of X-ray quality crystals of [Cr(tame)$(N_3)_3$] · H_2O. Anal. Calcd for $C_5H_{17}N_{12}CrO$: C, 19.2; H, 5.5; N, 53.6; Cr, 16.6. Found: C, 19.4; H, 5.6; N, 52.9; Cr, 16.5. (λ (nm), ε $(M^{-1}cm^{-1}))_{max}$ (in dimethyl sulfoxide (dmso)): (551, 149), (417, 128).

2.1.2. [Cr(tacn)$(N_3)_3$] (2). 0.20 g (0.30 mmol) of [Cr(tacn)$(OH_2)_3$]$(CF_3SO_3)_3$ and 0.20 g (3.1 mmol) of NaN_3 were dissolved in 2 cm^3 of water. The resulting violet solution was left overnight for crystallization. The red-violet crystals were washed with water and ethanol and then dried in air. Yield: 85 mg (92%) of X-ray quality crystals of [Cr(tacn)$(N_3)_3$]. Anal. Calcd for $C_6H_{15}N_{12}Cr$: C, 23.5; H, 4.9; N, 54.7; Cr, 16.9. Found: C, 23.6; H, 5.1; N, 54.3; Cr, 16.5. (λ (nm), ε $(M^{-1}cm^{-1}))_{max}$ (in dmso): (561, 177), (425, 123).

2.1.3. [Cr(tame)$(NCCH_3)_3$]$(BF_4)_3$ (3). 55 mg (0.64 mmol) of [Cr(tame)$(N_3)_3$] · H_2O was added in small portions to a solution of 100 mg (0.86 mmol) $NOBF_4$ in 1 cm^3 CH_3CN. Gas evolution was observed and the solution became yellow. Then 5 cm^3 of diethyl ether was added. The resulting yellow precipitate was filtered off and washed with diethyl ether and dried *in vacuo*. Yield: 64 mg (82%) of [Cr(tame)$(NCCH_3)_3$]$(BF_4)_3$. Anal. Calcd for $C_{11}H_{24}N_6B_3CrF_{12}$: C, 23.9; H, 4.4; N, 15.2; Cr, 9.4. Found: C, 23.6; H, 4.7; N, 14.9; Cr, 9.5. (λ (nm), ε $(M^{-1}cm^{-1}))_{max}$ (in CH_3CN): (456, 53), (349, 55).

2.1.4. [Cr(tacn)(NCCH$_3$)$_3$](BF$_4$)$_3$ (4). Made as **3** from **2** in 90% yield. Anal. Calcd for $C_{12}H_{24}N_6B_3CrF_{12}$: C, 25.5; H, 4.3; N, 14.9; Cr, 9.2. Found: C, 25.4; H, 4.5; N, 14.6; Cr, 9.0. (λ (nm), ε ($M^{-1}cm^{-1}$))$_{max}$ (in CH_3CN): (457, 90), (348, 36).

2.2. *X-ray crystallography*

Intensity data were collected at 122 K on a Bruker–Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream and graphite monochromatized Mo-Kα radiation. Data were reduced with EvalCCD [11], the structures solved by direct methods using SIR97 [12] and refined by least-squares against F^2 with SHELXL97 [13] as incorporated in the maXus program [14]. Complex **1** co-crystallized, with one water molecule in the asymmetric unit, as a racemic mixture in the centro-symmetric space group $P2_1/c$. Complex **2** also crystallized as a racemic mixture in space group $P\bar{1}$ with one complex per asymmetric unit. Crystallographic parameters and statistics are summarized in table 1. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were found in subsequent difference Fourier maps and refined using a riding model. Due to the crystal content of chromium, numerical absorption corrections were performed for both sets of intensity data.

Table 1. Crystal data and refinement details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$CrC_5H_{17}N_{12}O$	$CrC_6H_{15}N_{12}$
M_r	313.31	307.30
T (K)	122(2)	122(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.2460(9)	7.698(4)
b (Å)	11.0500(11)	8.5800(6)
c (Å)	13.1980(9)	10.236(3)
α (°)	90	89.497(15)
β (°)	97.244(7)	83.70(2)
γ (°)	90	72.83(2)
V (Å^3)	1337.7(2)	641.8(4)
Z	4	2
ρ_{Calcd} (g cm^{-3})	1.556	1.590
$\mu_{Mo\text{-}K\alpha}$ (mm^{-1})	0.872	0.902
F(000)	652	318
Crystal size (mm^3)	0.55 × 0.12 × 0.11	0.47 × 0.18 × 0.05
θ range (°)	2.22–40.98	2.49–35.10
Reflections collected	63,561	30,099
Unique data	8817 [$R_{int}=0.0598$]	5674 [$R_{int}=0.0513$]
Obsd reflections [$I>2\sigma(I)$]	6852	5674
Goodness-of-fit on F^2	1.079	1.038
R indices (all data)	$R_1=0.0540$, $wR_2=0.0743$	$R_1=0.0465$, $wR_2=0.0837$
Larg. diff. peak/hole (e Å^{-3})	0.447/−0.791	0.611/−0.550

2.3. *Other physical measurements*

Optical absorption spectra were recorded on a Cary 5E UV-Vis-NIR spectrophotometer. Continuous photolysis was carried out on stirred solutions in a square quartz cuvette with a 1.000 cm path-length on an optical train using collimated light from a 200 W Hg lamp. Elemental analyses were done at the Microanalytical Laboratory in our department.

3. Results and discussion

The preparation of **1** and **2** is outlined in scheme 1. Triflate anions ($CF_3SO_3^-$) coordinated to a metal center are easily displaced by other ligands and triflato complexes have thus been used extensively as synthetic precursors [15]. The present triflato complexes were conveniently prepared in high yields by reaction between the chloro complexes and triflic acid. The resulting triflato complexes, being inner complexes, are insoluble in water but easily soluble in acetone, and the hydrolysis can thus be performed in acetone containing a little water. The final substitution of water ligands with azide is slow at room temperature, and this secures the formation of large crystals of **1** and **2**.

$$[Cr(L_3)Cl_3] \xrightarrow{CF_3SO_3H} [Cr(L_3)(CF_3SO_3)_3] \xrightarrow{H_2O}$$

$$[Cr(L_3)(OH_2)_3](CF_3SO_3)_3 \xrightarrow{NaN_3} [Cr(L_3)(N_3)_3] \qquad L_3 = \text{tame or tacn}$$

Scheme 1. Synthetic steps in the prepartions of **1** and **2**.

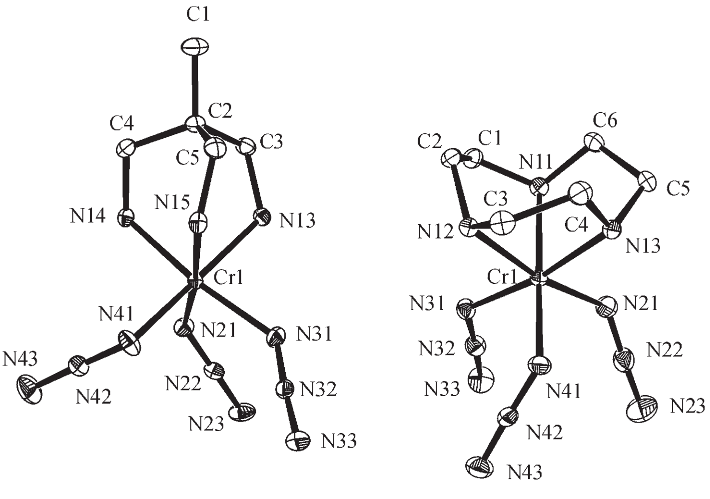
The nitrosation of azido complexes can take place in water by using HNO_2 (equation (1)) or in non-aqueous solvents such as CH_3CN (equation (2)) by use of salts of the nitrosonium ion, such as $NOBF_4$ or $NOPF_6$.

$$Cr{-}N_3^{q+} + HNO_2 + H^+ \rightarrow Cr{-}OH_2^{(q+1)+} + N_2O + N_2 \tag{1}$$

$$Cr{-}N_3^{q+} + NO^+ + CH_3CN \rightarrow Cr{-}NCCH_3^{(q+1)+} + N_2O + N_2 \tag{2}$$

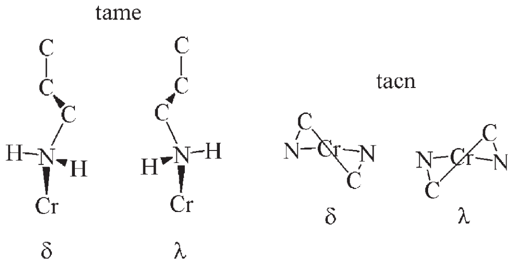
Earlier studies of nitrosation of the *mer* and *fac* isomers of $[Cr(NH_3)_3(N_3)_3]$ show that such reactions occur stereoretentively [8, 16]. In the cases of **1** and **2** nitrosation in CH_3CN gives the tris(acetonitrile) complexes **3** and **4**. Being easily soluble in organic solvents, **3** and **4** might serve as useful entries into the chemistry in non-aqueous media.

The Cr(III) ion in **1** is octahedrally coordinated to three nitrogen atoms of the tridentate, tripodal amine ligand and to three azido groups, each bounded end-on as seen in figure 1. The amine ligand coordinates to the chromium(III) ion with a three-fold axis through the metal center giving a facial configuration. The conformation of the amine ligand can be described by the orientation of the $(H_2)C$–N bond relative to the three-fold axis (i.e., δ or λ, see scheme 2). The δ enantiomer of the racemate is shown in figure 1. The packing of the unit cell is shown in figure 2. The Cr–N(amine) and Cr–N(azide) distances are in good agreement with those found in other amine and azide complexes of chromium(III) [2, 8, 17]. The coordination geometry in **2** is similar, with a facially coordinated tacn ligand as seen in figure 1. The conformation of the

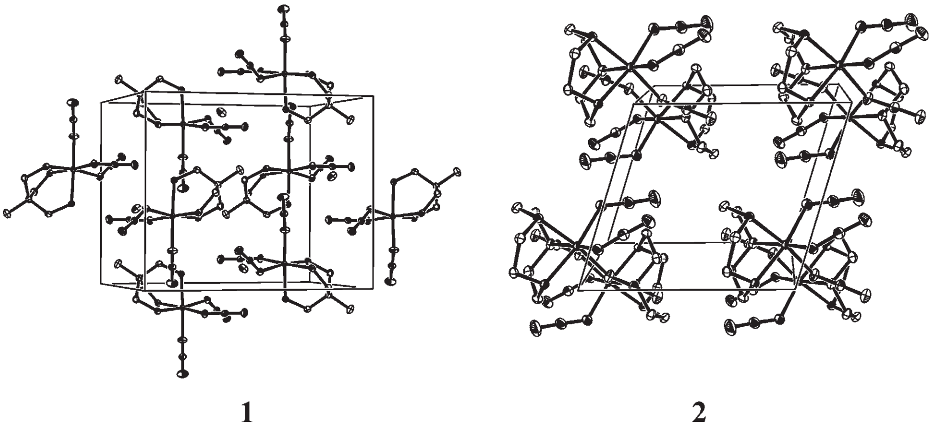


1 **2**

Figure 1. ORTEP drawings of **1** and **2**. The thermal ellipsoids enclose 50% probability.



Scheme 2. Illustration of the conformations of **1** and **2**.



1 **2**

Figure 2. ORTEP drawing of the packing in the unit cell for **1** and **2**.

Table 2. Selected interatomic distances (Å) and angles (°) in **1**.

Cr1–N13	2.0821(7)	N13–Cr1–N14	85.56(3)
Cr1–N14	2.0669(7)	N13–Cr1–N15	87.93(3)
Cr1–N15	2.0662(7)	N14–Cr1–N15	87.88(3)
Cr1–N21	2.0349(7)	N13–Cr1–N41	174.70(3)
Cr1–N31	2.0237(7)	N14–Cr1–N31	170.91(3)
Cr1–N41	2.0182(8)	N15–Cr1–N21	173.58(3)

Table 3. Selected interatomic distances (Å) and angles (°) in **2**.

Cr1–N11	2.0776(11)	N11–Cr1–N12	81.74(5)
Cr1–N12	2.0964(12)	N11–Cr1–N13	81.79(4)
Cr1–N13	2.0841(11)	N12–Cr1–N13	81.22(4)
Cr1–N21	1.9906(14)	N11–Cr1–N41	171.16(4)
Cr1–N31	2.0105(11)	N12–Cr1–N21	169.94(4)
Cr1–N41	2.0226(12)	N13–Cr1–N31	171.36(4)

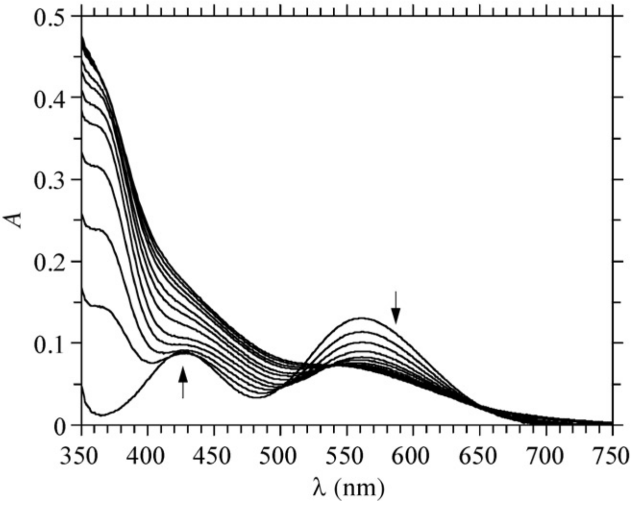


Figure 3. Optical absorption spectra recorded during the continuous photolysis ($\lambda = 365$ nm) of a 7.4×10^{-4} M solution of **2** in dmso. The spectra were recorded after 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 and 22 min photolysis.

tacn ligand can be either *δδδ* or λλλ with the λλλ enantiomer of the racemate shown in figure 1. In **1** and **2** the azide groups are asymmetric, the longer bond being between the central nitrogen atom and the nitrogen atom coordinated to the metal (averagely 0.042 Å longer). This is generally observed in azide complexes. The Cr–N–N angles (124.4–129.9°) are normal for end-on coordinated azide groups and the N–N–N angles are close to the ideal 180°. Selected interatomic distances and bond angles are shown in tables 2 and 3.

The optical absorption spectra of **1**–**4** display two ligand field bands in the visible range: ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (lowest energy) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$. In a d^3 complex with the O_h symmetry the spin allowed transition ${}^4A_{2g} \rightarrow {}^4T_{2g}$ is equal to the ligand field parameter Δ_o. For a *fac*-[Cr^{III}A$_3$B$_3$] chromophore with the holohedrized symmetry O_h, the energy of this transition will thus be the average of the values of Δ_o in the [Cr^{III}A$_6$]

and $[\mathrm{Cr^{III}B_6}]$ chromophores. From the literature the values for Δ_o in $[\mathrm{Cr(tacn)_2}]^{3+}$ [18], $[\mathrm{Cr(NCCH_3)_6}]^{3+}$ [19] and $[\mathrm{Cr(N_3)_6}]^{3-}$ [20] can be found to be $22.8 \times 10^3\,\mathrm{cm^{-1}}$, $20.2 \times 10^3\,\mathrm{cm^{-1}}$ and $15.0 \times 10^3\,\mathrm{cm^{-1}}$, respectively. The complex $[\mathrm{Cr(tame)_2}]^{3+}$ has not been reported. This gives the calculated values for the lowest energy transition for complexes **2** and **4** to be $18.9 \times 10^3\,\mathrm{cm^{-1}}$ and $21.5 \times 10^3\,\mathrm{cm^{-1}}$ in fair agreement with the experimental values, which are $17.8 \times 10^3\,\mathrm{cm^{-1}}$ and $21.9 \times 10^3\,\mathrm{cm^{-1}}$, respectively.

Preliminary work has shown that dmso solutions of **1** and **2** are light sensitive with the violet solution eventually becoming yellow upon irradiation with UV-light (figure 3). Wieghardt [2, 3] has observed a photorelease of dinitrogen from azidochromium(III) complexes with formation of chromium(V) nitrido complexes (equation (3)).

$$\mathrm{Cr{-}N_3^{q+}} \xrightarrow{h\nu} \mathrm{Cr{\equiv}N^{q+}} + \mathrm{N_2} \qquad (3)$$

On this background we are currently investigating the nature of the product(s) formed on photolysis of **1** and **2**.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary data (CCDC 640167 for **1** and CCDC 640168 for **2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033, or Email: deposit@ccdc.cam.ac.uk).

References

[1] S.I. Arshankow, A.L. Poznjak. *Z. Anorg. Allg. Chem.*, **481**, 201 (1981).
[2] K. Meyer, J. Bendix, E. Bill, T. Weyhermüller, K. Wieghardt. *Inorg. Chem.*, **37**, 5180 (1998).
[3] A. Niemann, U. Bossek, G. Haselhorst, K. Wieghardt, B. Nuber. *Inorg. Chem.*, **35**, 906 (1996).
[4] A. Haim, H. Taube. *Inorg. Chem.*, **2**, 1199 (1963).
[5] R.B. Jordan, A.M. Sargeson, H. Taube. *Inorg. Chem.*, **5**, 1091 (1966).
[6] D.G. Butler, I.I. Creaser, S.F. Dyke, A.M. Sargeson. *Acta Chem. Scand.*, **A32**, 789 (1978).
[7] I.I. Creaser, J.M. Harrowfield, F.R. Keene, A.M. Sargeson. *J. Am. Chem. Soc.*, **103**, 3559 (1981).
[8] A. Døssing, P. Engberg, R. Hazell. *Acta Chem. Scand.*, **51**, 849 (1997).
[9] K. Wieghardt, W. Schmidt, H. Endres, C.R. Wolfe. *Chem. Ber.*, **112**, 2837 (1979).
[10] P. Andersen, H. Matsui, K.M. Nielsen, A.S. Nygaard. *Acta Chem. Scand.*, **48**, 542 (1994).
[11] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs. *J. Appl. Cryst.*, **36**, 220 (2003).
[12] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).
[13] G.M. Sheldrick. *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[14] S. Mackey, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland. *MaXus: Computer Program for the Solution and Refinement of Crystal Structures*, The University of Glasgow, Bruker Nonius, The Netherlands, Macscience, Japan (1999).
[15] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson. *Inorg. Chem.*, **23**, 2940 (1984).
[16] A. Døssing. *Acta Chem. Scand.*, **48**, 269 (1994).
[17] M.A.S. Goher, M.A.M. Aby-Youssef, F.A. Mautner. *Z. Naturforsch.*, **B47**, 139 (1992).
[18] K. Wieghardt, W. Schmidt, W. Herrmann, H.J. Küppers. *Inorg. Chem.*, **22**, 2953 (1983).
[19] O. Hatlevik, A.M. Arif, J.S. Miller. *J. Phys. Chem. Solids*, **65**, 61 (2004).
[20] W. Beck, W.P. Fehlhammer, P. Pöllmann, E. Schuierer, K. Feldl. *Chem. Ber.*, **100**, 2335 (1967).