Two $[Nb_6Cl_9O_3(CN)_6]^{5-}$ Isomer Anions in Two Nb_6 Cluster Oxyhalides: $Cs_5[Nb_6Cl_9O_3(CN)_6]\cdot 4\,H_2O$ and $(Me_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot 5\,H_2O$**

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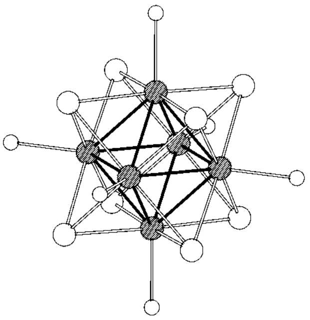
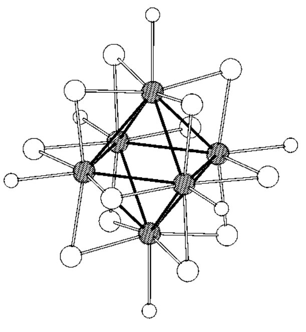
The $(M_6X_8)^{n+}$ and $(M_6X_{12})^{n+}$ cluster cores (M = transition metal; X = halogen, chalcogen) constitute the basic building blocks of the early transition metal cluster chemistry.[1–4] These $(M_6X_8)^{n+}$ and $(M_6X_{12})^{n+}$ entities are characterized by an M_6 octahedral cluster that is face-capped or edge-bridged by μ_3 or μ_2 inner ligands X^i. The clusters are stabilized by six additional ligands X^a in terminal positions to form $[M_6X^i_8X^a_6]^{n-}$ and $[M_6X^i_{12}X^a_6]^{n-}$ units. In mixed-ligand compounds, the fact that the M_6 cluster is bonded to ligands of different sizes and charges should lead to great distortions and various electronic counts, which in turn affect the properties of the cluster itself.



$[M_6X^i_8X^a_6]^{n-}$



$[M_6X^i_{12}X^a_6]^{n-}$

Up to now, a large number of $(M_6X_8)^{n+}$ cluster core isomers have been obtained in chalcohalide chemistry. With few exceptions[5,6] the crystallographic ligand sites are randomly occupied by halogen and chalcogen atoms; thus, the isomers are orientationally disordered.[7–9] Furthermore, such complexes exhibit the same valence electron count for the cluster (VEC = 24). In contrast, the Nb_6 and Ta_6 oxyhalides recently obtained, which were built from $(M_6X_{12})^{n+}$ cluster cores, provide mixed-ligand cluster phases with an ordered distribution of oxygen and halogen atoms at inner ligand positions. Hitherto, a series of solids containing different isomer cluster cores such as $(Nb_6Cl_{12-m}O_m)^{n+}$ (m = 1–4), $(Nb_6Cl_6O_6)^{n+}$, and $(Ta_6X_9O_3)^{n+}$ (X = Cl, Br) have been described.[10–12] Their structures are based on $[M_6X^i_{12}X^a_6]^{n-}$ units containing a distorted M_6 cluster with various electronic counts (VEC = 14–16). Recently, the first W_6 oxychlorides based on the same type of unit were isolated.[13] All these compounds are prepared by standard solid-state routes, that is, stoichiometric reactions in sealed quartz tubes at 650–850 °C. They are insoluble in water and common organic solvents.

The aim of the present work was to synthesize oxyhalide cluster isomers and to characterize them in solution and in the solid state in order to determine the influence of the position of oxygen in the cluster core on the structural and physical properties. Further, the clusters could be used as starting materials to design new inorganic polymeric cluster materials of different dimensionality.[14]

To this purpose we have investigated the interaction of the solid-state niobium cluster oxyhalides $Cs_2LaNb_6Cl_{15}O_3$[11d] and $ScNb_6Cl_{13}O_3$[11a]—each contains a $(Nb_6Cl^i_9O^i_3)^{n+}$ cluster core that differs by the distribution of the three oxygen atoms at the inner positions—with aqueous KCN solution to replace the apical chlorine atom by a CN^- ligand. In this reaction, the $(Nb_6Cl^i_9O^i_3)^{n+}$ cluster core was expected to be unchanged, as observed for $(M_6X^i_8)^{n+}$ in transition metal octahedral cluster chemistry.[15] Accordingly, we have now isolated the soluble salts $Cs_5[Nb_6Cl_9O_3(CN)_6]\cdot 4\,H_2O$ (**1**) and $(Me_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot 5\,H_2O$ (**2**) containing $[Nb_6Cl_9O_3(CN)_6]^{5-}$ isomer anions that have been "excised" from the starting materials.

The niobium clusters $Cs_2LaNb_6Cl_{15}O_3$ and $ScNb_6Cl_{13}O_3$ react with deoxygenated aqueous solutions of KCN at room temperature. The solids fully dissolve to give green-brown solutions of $[Nb_6Cl^i_9O^i_3(CN)^a_6]^{5-}$ anions. The insoluble residues do not contain any traces of starting materials. The solutions and crystals of **1** and **2** are quite stable under an inert atmosphere but quickly decompose when exposed to air to give white hydrated niobium oxide(v) $Nb_2O_5\cdot x\,H_2O$. This decomposition is accelerated after addition of organic solvents—such as DMF, acetonitrile, methanol, or ethanol—containing traces of dissolved oxygen.

The excision reaction did not change the composition and ligand distribution of the $(Nb_6Cl^i_9O^i_3)^{n+}$ cluster cores observed in the parent oxychlorides. The $[Nb_6Cl^i_9O^i_3(CN)^a_6]^{5-}$ anions in **1** and **2** have a typical M_6X_{18} niobium octahedral cluster arrangement. The three oxygen and nine chlorine atoms are ordered over the 12 μ_2 positions, but their distribution in the two anions is strictly different (Figure 1). While in **1** the $Nb_6Cl^i_9O^i_3$ cluster core has an idealized D_3 symmetry, in **2** it has C_2 symmetry. The Nb–Nb, Nb–Cl, and Nb–O distances in **1** and **2** are very close to the corresponding distances in the two starting materials. The mean Nb–O distance is 1.952 Å for **1** and 2.006 Å for **2**, while the mean Nb–Cl distance is 2.493 Å for **1** and 2.492 Å for **2**. The difference between the sizes of the oxygen and chlorine atoms results in a large distortion of the Nb_6 cluster. Indeed, the Nb–Nb distances range from 2.790(2) to 2.9979(15) Å in **1** and from 2.7817(15) to 3.0251(15) Å in **2**. The shortest Nb–Nb distances of 2.790(2) Å for **1** and 2.7817(15) Å for **2** are seen for the oxygen-bridged edges of the octahedrons; these are comparable to the corresponding distances in octahedral niobium oxychlorides and ox-

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[**] This work was supported by INTAS (grant N2000-00689). N.G.N. is grateful to the NATO for financial support during his stay at the LCSIM. The authors thank the Center of Diffractometry of Rennes 1 University for crystal structures and the Center for Scanning Electron Microscopy and Microanalyses of Rennes 1 University for analyses.

ides.[11,12,16] The differences in the Nb–Nb distances result in a distortion of the outer ligand environment.[17]

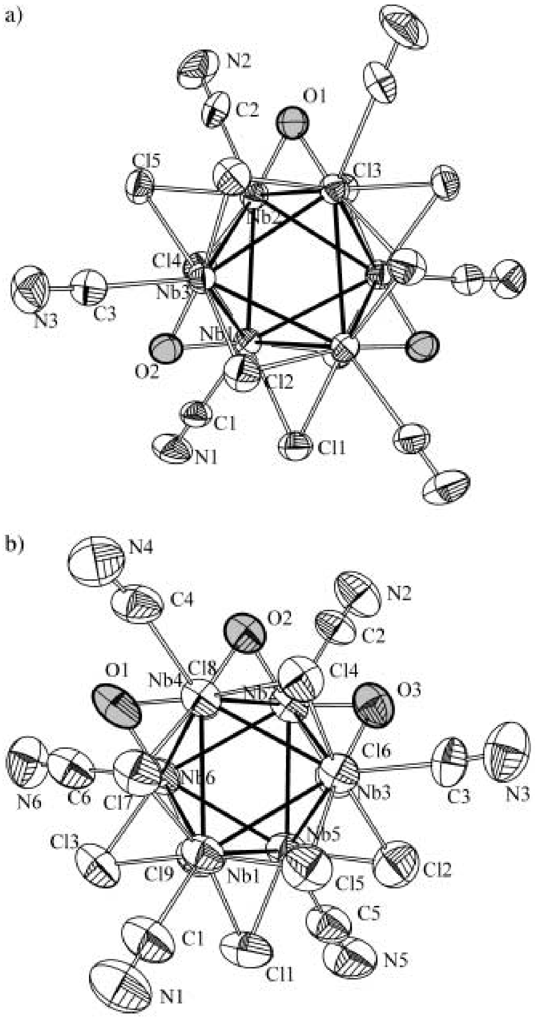

Figure 1. Structure of the $[Nb_6Cl_9O_3(CN)_6]^{5-}$ anion in a) **1** and b) **2**.

In **1** all three crystallographically independent niobium atoms lie in a similar environment made up of one μ_2 oxygen atom, three μ_2 chlorine atoms, and one terminal CN^- ligand. On the other hand, in **2** each of the two crystallographically independent $[Nb_6Cl_9O_3(CN)_6]^{5-}$ anions contain three kinds of Nb atoms which show a different coordination sphere: Nb1, Nb6 (Nb7, Nb12) are surrounded by four Cl atoms, Nb3, Nb4 (Nb9, Nb10) by three Cl and one O atoms, and Nb2, Nb4 (Nb8, Nb11) by two Cl and two O atoms. Additionally each niobium atom is coordinated by a terminal CN^- group.

The mean Nb–C distances of 2.33 Å for **1** and 2.31 Å for **2** are slightly longer than those found in $[Nb(CN)_8]^{5-}$ (2.282, 2.242 Å),[18a] $[Nb(CN)_8]^{4-}$ (2.225 Å),[18b] and $[Nb_4OTe_4(CN)_{12}]^{6-}$ (2.225 Å).[18c] This point could be explained by the decrease in the formal charge of the Nb atom in the title compounds in terms of the ionic model. For **1** and **2**, the valence electron count per cluster is calculated to be 14, as in the starting compounds. This result evidences that no redox process occurs during the excision reaction.

Previous theoretical studies of the bonding situation in the D_3 and C_2 $[(Nb_6Cl^i_9O^i_3)Cl^a_6]^{n-}$ cluster isomers have provided further evidence for the differences in the electronic structures. In particular, different HOMO–LUMO energy gaps were found for the D_3 and C_2 isomers (1.456 and 0.607 eV, respectively).[19] Different electronic properties are expected for the CN^--substituted isomers. Indeed, the electronic absorption spectra for the D_3 and C_2 isomers exhibit band maxima that are shifted with respect to one another (Figure 2). The IR spectrum of **1** shows one CN^- stretching vibration of medium intensity at 2111 cm^{-1}, which corresponds to one type of Nb center linked by a CN^- group. For **2**, the IR spectra present two vibrations at 2116 and 2132 cm^{-1} with a relative intensity of 2:1, which relates to the presence of niobium atoms with different environments containing μ_2 ligands.[20]

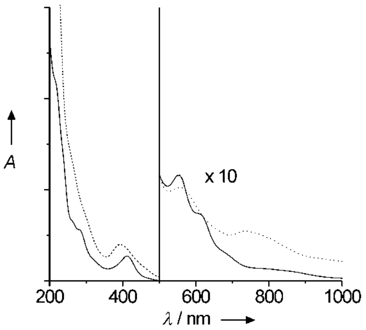

Figure 2. Electronic absorption spectra for **1** (solid line) and **2** (dashed line) resulting from the two different isomers of the $[Nb_6Cl_9O_3(CN)_6]^{5-}$ anion. The absorption *A* is given in arbitrary units.

In conclusion, the interaction of the octahedral niobium clusters $Cs_2LaNb_6Cl_{15}O_3$ and $ScNb_6Cl_{13}O_3$ with a cyanide solution resulted in excision of the cluster cores and isolation of two $[Nb_6Cl_9O_3(CN)_6]^{5-}$ isomer anions. The reactions proceed under mild conditions with no exchange of inner ligands. This approach could be expanded to other mixed-ligand octahedral halides and oxyhalides of niobium and tantalum. These anions could serve as a virtual library of anions for the construction of new cluster solids.

Experimental Section

All experiments were carried out under an argon atmosphere and with deoxygenated solutions. For the structure analyses, single crystals were selected directly from the reaction products. The data were collected on a Nonius KappaCCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods and refined against all data using SHELXL-97.[21]

$Cs_5[Nb_6Cl_9O_3(CN)_6]\cdot 4H_2O$ (**1**):[22] $Cs_2LaNb_6Cl_{15}O_3$[11d] (200 mg, 0.130 mmol) was added to 50 mL of an aqueous solution of KCN (127 mg, 1.95 mmol) and CsCl (570 mg, 3.39 mmol), and the mixture was stirred for 24 h. The resulting green-brown solution was filtered, and the filtrate was reduced in volume under vacuum at ambient temperature to 5 mL and then added to 50 mL of ethanol. Dark-brown crystals were collected by filtration, washed with ethanol, and dried under argon. Yield: 142 mg (60%). EDAX: Cs:Nb:Cl = 4.9:6.0:8.9; IR: $\tilde{\nu} = 2111$ cm^{-1} (CN^-); UV-Vis: λ (ε) = 220 (30000), 245sh (18900), 263 (8980), 286 (7500), 420 (3600), 555 (580), 612 (410), 680sh (195), 800br (85). Crystallographic analysis: The crystal for X-ray structure analysis was grown by slow evaporation of a solution of **1** in a desiccator under Ar. Dark-brown crystals formed within several days together with mixed crystals of KCl/KCN and were collected manually.

$C_3Cl_{4.50}Cs_{2.50}N_3Nb_3O_{3.50}$, $T = 293$ K, orthorhombic, space group $C222_1$; $a = 8.7854(3)$, $b = 23.9393(8)$, $c = 18.0270(8)$ Å; $V = 3791.4(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.170$ g cm^{-3}, $R_1 = 0.0516$, $wR_2 = 0.1016$ for 3143 data (19433 independent), 205 parameters with no restraints. The Cs cations were split over several closely spaced sites. Only positions with high occupancy were refined anisotropically.

$(Me_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot 5H_2O$ (**2**):[22] $ScNb_6Cl_{13}O_3$[11a] (200 mg, 0.180 mmol) was added to 40 mL of an aqueous solution of KCN (176 mg, 2.70 mmol) and Me_4NCl (592 mg, 5.4 mmol), and the mixture was stirred for 24 h. The volume was reduced under vacuum at ambient temperature to 5 mL and allowed to dry in a dessicator over silica gel under Ar. Dark brown crystals were collected manually from the reaction mixture. Yield: 153 mg (55 %). EDAX: Nb:Cl = 6.0:9.1; IR $\tilde{\nu} = 2116$, 2132 cm^{-1} (CN^-); UV-Vis: λ (ε) = 220 (28000), 245sh (9700), 300sh (5170), 390 (2800), 560 (540), 730 (275), 760sh (270). Crystallographic analysis: $C_{52}H_{120}Cl_{18}N_{22}Nb_{12}O_{14}$, $T = 293$ K, monoclinic, space group Pc; $a = 12.27900(10)$, $b = 12.64800(10)$, $c = 37.695(2)$ Å; $\beta = 100.231(9)°$, $V = 5761.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.747$ g cm^{-3}, $R_1 = 0.0645$, $wR_2 = 0.1532$ for 15169 data (20879 independent), 998 parameters with 27 restraints. The crystal of **2** was a racemic twin (Flack parameter 0.53(7)). A portion of the tetramethylammonium cations have a high displacement factor and their geometry was fixed by restaints. Solvent water molecules were disordered over multiple positions in the structure.

$(Et_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot xH_2O$: Addition of an excess of Et_4NCl to a solution of **1** and slow evaporation resulted in crystallization of $(Et_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot xH_2O$. EDAX: K:Nb:Cl = 0.02:6.0:8.9; FAB MS$^+$: M/z: 1861.11 $\{(Et_4N)_6[Nb_6Cl_9O_3(CN)_6]\}^+$. Crystallographic analysis: The structure and bond lengths of the $[Nb_6Cl_9O_3(CN)_6]^{5-}$ anion in $(Et_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot xH_2O$ are very similar to that found in **1**. The tetraethylammonium cations and water molecules were strongly disordered, and we were not able to achieve a satisfactory R value. Space group: $I432$, $a = 24.8199(4)$ Å, $V = 15289.7(4)$ Å^3, $Z = 8$, $R_1 = 0.124$. Selected bond distances (Å): av Nb–Nb 2.95 (μ_2-Cl bridge), av Nb–Nb 2.89 (μ_2-O bridge), Nb–O 2.10(1), av Nb–Cl 2.46, Nb–C 2.30(1), C–N 1.10(1).

Received: February 18, 2002 [Z18721]

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[1] a) J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603–4616; b) N. Prokopuk, D. F. Shriver, *Adv. Inorg. Chem.* **1999**, *46*, 1–49; c) T. Saito, *J. Chem. Soc. Dalton Trans.* **1999**, 97–105, and references herein.

[2] A. Simon, *Clusters and Colloids. From Theory to Applications* (Ed.: G. Schmidt), VCH, Weinheim, **1994**.

[3] J. D. Corbett, *J. Alloys Compd.* **1995**, *229*, 10–23.

[4] C. Perrin in *Metal Cluster in Chemistry, Vol. 3* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, pp. 1563–1590.

[5] C. Perrin, R. Chevrel, M. Sergent, O. Fischer, *Mater. Res. Bull.* **1979**, *14*, 1505–1515.

[6] C. Perrin, M. Potel, M. Sergent, *Acta Crystallogr. Sect. C.* **1983**, *39*, 415–418.

[7] C. Perrin, M. Sergent, F. Le Traon, A. Le Traon, *J. Solid State Chem.* **1978**, *25*, 197–204.

[8] A. Perricone, A. Slougui, A. Perrin, *Solid State Sci.* **1999**, *1*, 657–666.

[9] J. C. P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, *Chem. Rev* **2001**, *101*, 2037–2066, and references herein.

[10] S. Cordier, F. Gulo, C. Perrin, *Solid State Sci.* **1999**, *1*, 637–646.

[11] a) S. Cordier, C. Perrin, M. Sergent, *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 1049–1060; b) S. Cordier, C. Perrin, M. Sergent, *J. Solid State Chem.* **1995**, *120*, 43–48; c) S. Cordier, C. Perrin, M. Sergent, *Mater. Res. Bull.* **1996**, *31*, 683–690; d) S. Cordier, C. Perrin, M. Sergent, *Mater. Res. Bull.* **1997**, *32*, 25–33; e) F. Gulo, C. Perrin, *J. Mater. Chem.* **2000**, *10*, 1721–1724; f) F. Gulo, T. Roisnel, C. Perrin, *J. Mater. Chem.* **2001**, *11*, 1237–1241; g) F. Gulo, C. Perrin, *J. Solid State Chem.*, in press.

[12] a) E. V. Anokhina, M. W. Essig, A. Lachgar, *Angew. Chem.* **1998**, *110*, 538–540; *Angew. Chem. Int. Ed.* **1998**, *37*, 522–525; b) E. V. Anokhina, C. S. Day, A. Lachgar, *Chem. Commun.* **2000**, 1491–1492; c) E. V. Anokhina, C. S. Day, M. W. Essig, A. Lachgar, *Angew. Chem.* **2000**, *112*, 1089–1091; *Angew. Chem. Int. Ed.* **2000**, *39*, 1047–1049; E. V. Anokhina, C. S. Day, A. Lachgar, *Inorg. Chem.* **2001**, *40*, 5072–5076.

[13] N. R. M. Crawford, J. R. Long, *Inorg. Chem.* **2001**, *40*, 3456–3462.

[14] a) N. G. Naumov, A. V. Virovets, M. N. Sokolov, S. B. Artemkina, V. E. Fedorov, *Angew. Chem.* **1998**, *110*, 2043–2045; *Angew. Chem. Int. Ed.* **1998**, *37*, 1943–1945; b) N. G. Naumov, D. V. Soldatov, J. A. Ripmeester, S. B. Artemkina, V. E. Fedorov, *Chem. Commun.* **2001**, 571–572, and references herein; c) M. V. Bennett, L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2001**, *123*, 8022–8032, and references herein.

[15] For M = Re: a) Y. V. Mironov, J. A. Cody, T. E. Albrecht-Schmitt, J. A. Ibers, *J. Am. Chem. Soc.* **1997**, *119*, 493–498; b) N. G. Naumov, A. V. Virovets, N. V. Podberezskaya, V. E. Fedorov, *J. Struct. Chem.* **1997**, *38*, 857–862; c) H. Imoto, N. G. Naumov, A. V. Virovets, T. Saito, V. E. Fedorov, *J. Struct. Chem.* **1998**, *39*, 720–727; d) V. E. Fedorov, S. V. Tkachev, N. G. Naumov, Yu. V. Mironov, Yu. I. Mironov, *Russ. J. Inorg. Chem.* **1998**, *43*, 1562–1572; e) L. G. Beauvais, M. P. Shores, J. R. Long, *Chem. Mater.* **1998**, *10*, 3783–3786; for M = Mo: f) Y. V. Mironov, A. V. Virovets, N. G. Naumov, V. N. Ikorskii, V. E. Fedorov, *Chem. Eur. J.* **2000**, *6*, 1361–1365; g) K. A. Brylev, A. V. Virovets, N. G. Naumov, Yu. V. Mironov, D. Fenske, V. E. Fedorov, *Russ. Chem. Bull.* **2001**, *50*, 1140–1143; h) C. Magliocchi, X. B. Xie, T. Hughbanks, *Inorg. Chem.* **2000**, *39*, 5000–5001; for M = W: i) S. Jin, F. J. DiSalvo, *Chem. Commun.* **2001**, 1586–1587.

[16] J. Koehler, G. Svensson, A. Simon, *Angew. Chem.* **1992**, *104*, 1463–1483; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1437–1456.

[17] This distortion was reflected by the value for the C-X-C angle (where X is the center of mass for the Nb_6 octahedron). These angles differ for Nb–Nb edges bridged by μ-O and μ-Cl atoms and are in the ranges of 79.5–82.6° (μ-O) and 92.0–94.0° (μ-Cl) for **1** and 80.5–85.9° (μ-O) and 87.5–94.1° (μ-O) for **2**.

[18] a) M. B. Hursthouse, A. M. Galas, *J. Chem. Soc. Chem. Commun.* **1980**, 1167–1168; b) M. Laing, G. Gafner, W. P. Griffith, P. M. Kiernan, *Inorg. Chim. Acta* **1979**, *33*, L119–120; c) V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, I. S. Neretin, Yu. L. Slovokhotov, *Chem. Commun.* **1998**, 2579–2580.

[19] F. Ogliaro, S. Cordier, J. F. Halet, C. Perrin, J. Y. Saillard, M. Sergent, *Inorg. Chem.* **1998**, *37*, 6199–6207.

[20] a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, **1997**, and references herein; b) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283–391, and references herein.

[21] a) G. M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1990**; b) G. M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**.

[22] CCDC-175878 and CCDC-175879 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).