

Homoleptic Alkaline Earth Metal Bis(trifluoromethanesulfonyl)imide Complex Compounds Obtained from an Ionic Liquid

Arash Babai and Anja-Verena Mudring*

Universität zu Köln, Institut für Anorganische Chemie, Greinstrasse 6, D-50939 Köln, Germany

Received October 21, 2005

The first homoleptic alkaline earth bis(trifluoromethanesulfonyl)imide (Tf_2N) complexes $[\text{mppy}r]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$, $[\text{mppy}r]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$, and $[\text{mppy}r][\text{Ba}(\text{Tf}_2\text{N})_3]$ were crystallized from a solution of the respective alkaline earth bis(trifluoromethanesulfonyl)imide and the ionic liquid $[\text{mppy}r][\text{Tf}_2\text{N}]$ ($\text{mppy}r = 1,1\text{-}N\text{-methyl-}N\text{-propylpyrrolidinium}$). In the calcium and strontium compounds, the alkaline earth metal (AE) is coordinated by four bidentately chelating Tf_2N ligands to form isolated (distorted) square antiprismatic $[\text{AE}(\text{Tf}_2\text{N})_4]^{2-}$ complexes which are separated by $N\text{-methyl-}N\text{-propylpyrrolidinium}$ cations. In contrast, the barium compound, $[\text{mppy}r][\text{Ba}(\text{Tf}_2\text{N})_3]$, forms an extended structure. Here the alkaline earth cation is surrounded by six oxygen atoms belonging to three Tf_2N^- anions which coordinate in a bidentate chelating fashion. Three further oxygen atoms of the same ligands are linking the Ba^{2+} cations to infinite $[\text{Ba}(\text{Tf}_2\text{N})_3]_\infty$ chains.

1. Introduction

Bis(trifluoromethanesulfonyl)imide (Tf_2N) compounds have gained considerable attention over the past few years. Extensive charge delocalization as well as the shape and especially the conformational flexibility renders the bis(trifluoromethanesulfonyl)imide anion (Tf_2N^-) as comparatively weakly coordinating.¹ Such bis(trifluoromethanesulfonyl)imides are attractive candidates for many electrochemical applications such as electrodeposition of electropositive metals, electrochemical capacitors, fuel cells, and batteries.² Because of its properties, the Tf_2N^- is able to significantly depress the melting points of tetraalkylammonium, N,N -dialkyl-pyrrolidinium, or N,N -dialkyl-imidazolium salts in such a way that room temperature ionic liquids (RTILs) are gained. This class of compounds is now widely used not only in electrochemistry but also in extraction chemistry and

especially as “green” solvents in organic synthesis and catalysis.³ Despite the strong interest and huge application of Tf_2N^- based RTILs, the interaction of metal centers with the ionic liquid so far lacks a deeper understanding, which is, however, critical for all kinds of applications. Moreover, X-ray structures of Tf_2N^- salts are relatively scarce because of the aforementioned high conformational flexibility and the weakly coordinating nature of the anion itself.

To elucidate the behavior of simple salts of divalent metals in Tf_2N -based RTILs, we have investigated the interaction of alkaline earth iodides MI_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{or Ba}$) in the ionic liquid $[\text{mppy}r][\text{Tf}_2\text{N}]$ (1,1- N -methyl-propylpyrrolidinium-bis(trifluoromethanesulfonyl)imide). Further motiva-

* To whom correspondence should be addressed. E-mail: a.mudring@uni-koeln.de. Fax: +49-221-470-5083.

- (1) (a) Wasserscheid, P.; Gordon, C. M.; Hilgers, C.; Mulddon, M. J.; Dunkin, I. R. *Chem. Commun.* **2001**, 1186. (b) Klingshirn, M. A.; Broker, G. A.; Holbrey, J. D.; Saughnessy, K. H.; Rogers, R. D. *Chem. Commun.* **2002**, 1394.
- (2) (a) Gorecki, W.; Jeannin, M.; Belorizki, F.; Roux, C.; Armand, M. J. *Phys.: Condens. Matter* **1995**, 7, 6823. (b) Bhatt, A. I.; May, I.; Volkovich, V. A.; Herherington, M. E.; Lewin, B.; Thied, R. C.; Ertok, N. J. *Chem. Soc., Dalton Trans.* **2002**, 4532. (c) Chen, P.-Y.; Hussey, C. L. *Electrochim. Acta* **2004**, 49, 5125. (d) Oldham, W. J., Jr.; Costa, D. A.; Smith, W. H. Industrial Applications for Green Chemistry. In *Ionic Liquids*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002. (e) Bhatt, A. I.; May, I.; Volkovich, V. A.; Collison, D.; Helliwell, M.; Polovov, I. B.; Lewin, R. G. *Inorg. Chem.* **2005**, 44, 4934.

- (3) (a) Industrial Applications for Green Chemistry. In *Ionic Liquids*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002. (b) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2002. (c) *Green Industrial Applications of Ionic Liquids*; Rogers, R. D., Seddon, K. R., Volkov, S., Eds.; Kluwer Academic Publishers: Norwell, MA, 2003. (d) *Ionic Liquids as Green Solvents, Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003. (e) *Ionic Liquids IIIa: Properties and Structures*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2005. (f) *Ionic Liquids as Green Solvents, Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003. (g) *Ionic Liquids IIIa: Transformation and Processes*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 902; American Chemical Society: Washington, DC, 2005. (h) *Ionic Liquids in Polymer Systems: Solvents, Additives, and Novel Applications*; Brazel, C. S., Rogers, R. D., Eds.; Oxford University Press: New York, 2005.

Table 1. Selected Crystallographic Data and Refinement Parameters

	[mppyr] ₂ [Ca(Tf ₂ N) ₄]	[mppyr] ₂ [Sr(Tf ₂ N) ₄]	[mppyr][Ba(Tf ₂ N) ₃]
empirical formula	C ₂₄ H ₃₆ CaF ₂₄ N ₆ O ₁₆ S ₈	C ₂₄ H ₃₆ SrF ₂₄ N ₆ O ₁₆ S ₈	C ₁₄ H ₁₈ BaF ₁₈ N ₄ O ₁₂ S ₆
fw	1417.15	1446.69	1106.02
cryst syst	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> (Å)	11.200(1)	11.488(1)	12.376(1)
<i>b</i> (Å)	22.447(3)	22.151(1)	24.043(1)
<i>c</i> (Å)	22.390(2)	23.534(1)	23.052(1)
β (deg)	107.74(1)	105.73(1)	
<i>V</i> (Å ³)	5361.6(1)	5764.8(6)	7144.7(6)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} (g cm ⁻³)	1.756	1.688	2.056
abs coeff (mm ⁻¹)	0.576	1.362	1.613
reflns collected	59083	78537	102336
independent reflns/ <i>R</i> _{int}	11669/0.1553	12677/0.0784	7984/0.0633
abs correction	numerical	numerical	numerical
<i>T</i> _{max} / <i>T</i> _{min}	0.9593/0.8120	0.8611/0.5515	0.8597/0.6502
params	857	716 (28 restraints)	498
GOF on <i>F</i> ²	0.818	0.904	1.001
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]: <i>R</i> ₁ , w <i>R</i> ₂	0.0543, 0.1057	0.0625, 0.1559	0.0281, 0.0625
<i>R</i> indices (all data): <i>R</i> ₁ , w <i>R</i> ₂	0.1673, 0.1414	0.1522, 0.1985	0.0456, 0.0691

tion for these studies came from our investigations of the spectroscopic and chemical behavior of divalent rare earth cations in this class of solvents⁴ as Ca²⁺ and Yb²⁺ as well as Sr²⁺ and Eu²⁺ have similar ionic radii. Thus alkaline earth cations are ideal model systems for the highly reducing divalent lanthanides.

2. Experimental Section

Synthesis. The ionic liquid 1,1-*N*-methyl-propylpyrrolidinium-bis(trifluoromethanesulfonyl)imide, [mppyr][Tf₂N], was prepared according to the literature procedure.⁵ The ionic liquid was dried for 120 h in a Schlenk tube at 150 °C under reduced pressure and rigorous stirring before use.

The alkaline earth iodides [AE]I₂, where AE = Ca, Sr, and Ba, were synthesized by dissolving the corresponding carbonate or oxide (99%, Merck) in aqueous HI (57%, Acros Organics). The anhydrous compound was obtained by removing the solvent and excess acid in high vacuum at 250 °C.

Storage and manipulation of the ionic liquid and the [AE]I₂ were carried out under drybox conditions (MBraun, Garching, Germany) and standard Schlenk techniques.

To synthesize [mppyr]₂[Ca(Tf₂N)₄], CaI₂ (0.17 mmol, 50 mg) and [mppyr][Tf₂N] (4 mmol, 1.63 g, ~1.1 mL) were placed in a silica tube which was sealed under vacuum. The reaction mixture was heated at 393 K for 48 h. Colorless transparent single crystals of [mppyr]₂[Ca(Tf₂N)₄] form as an insoluble product after the reaction mixture was cooled to room temperature (2 K/min). The product was separated by cannula-filtration from the ionic liquid. Estimated yield: 80%.

The analogous procedure with SrI₂ (1 mmol, 340 mg) and [mppyr][Tf₂N] (4 mmol, 1.63 g, ~1.1 mL) resulted in the formation of colorless transparent single crystals of [mppyr]₂[Sr(Tf₂N)₄] (estimated yield: 80%). BaI₂ (1 mmol, 390 mg) and [mppyr][Tf₂N] (4 mmol, 1.63 g, ~1.1 mL) gave [mppyr][Ba(Tf₂N)₃] in an estimated yield of 25%.

X-ray Crystal Structure Determination. All data were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite monochromated Mo K α radiation (λ = 0.710 73 Å) at 120(2) K (Ca), 170(2) K (Sr), and 170(2) K (Ba). While [mppyr]₂[Ca(Tf₂N)₄]

and [mppyr]₂[Sr(Tf₂N)₄] crystallize in the monoclinic crystal system, for [mppyr][Ba(Tf₂N)₃] an orthorhombic unit cell is observed. In the case of the calcium and the strontium compound, analysis of the reflection conditions led unambiguously to the space group *P*2₁/*c* (No. 15). The reflection conditions of the data set of the barium compound clearly indicated the space group *Pbca* (No. 61). Crystal structure solution by direct methods using SHELXS-97⁶ yielded in all cases the heavy atom positions. Subsequent difference Fourier analyses and least squares refinements with SHELXL-97⁷ allowed the localization of the remaining atom positions. In the case of [mppyr]₂[Ca(Tf₂N)₄], the hydrogen positions could be obtained from the difference Fourier map while for the other two compounds the hydrogen positions were calculated using the riding model. Crystal data and structure refinement parameters of the three structures are summarized in Table 1. Data reduction was carried out with the program package X-Red,⁸ and numerical absorption corrections were carried out with the program X-Shape.⁹ For crystal structure drawings the program Diamond was employed.¹⁰ Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, fax (+44)1223-336-033, e-mail deposit@ccdc.cam.ac.uk) on quoting the depository numbers CCDC-284996 ([mppyr]₂[Ca(Tf₂N)₄]), CCDC-284997 ([mppyr]₂[Sr(Tf₂N)₄]), and CCDC-284998 ([mppyr][Ba(Tf₂N)₃]), the authors, and the journal citation.

Raman Spectroscopy. Raman spectra were obtained from the bulk solids recorded at 150 mW on a Bruker IFS-FRA-106/s. For the measurement, the respective samples were sealed under an argon atmosphere in glass capillaries, and the data were recorded at room temperature.

[mppyr]₂[Ca(Tf₂N)₄]: 135(w), 212(w), 247(w), 291(m), 331(m), 353(m), 409(w), 553(w), 574(w), 746(vs), 902(m), 1041(w), 1149(m), 1246(s), 1329(m), 1454(s) cm⁻¹.

[mppyr]₂[Sr(Tf₂N)₄]: 133(w), 208(w), 239(w), 289(m), 329(m), 353(m), 409(w), 553(w), 574(w), 744(vs), 902(m), 1045(w), 1145(m), 1242(s), 1327(m), 1454(s) cm⁻¹.

(6) Sheldrick, W. S. *SHELXS-97*; Universität Göttingen: Göttingen, Germany, 1997.

(7) Sheldrick, W. S. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.

(8) *X-RED*; Stoe & Cie: Darmstadt, Germany, 2002.

(9) *X-Shape*; Stoe & Cie: Darmstadt, Germany, 2002.

(10) *Diamond*, version 2.1e; Crystal Impact GbR: Bonn, Germany, 1996–2001.

(4) Mudring, A.-V.; Babai, A.; Arenz, S.; Giernoth, R. *Angew. Chem.* **2005**, *117*, 5621 (*Angew. Chem., Int. Ed.* **2005**, *44*, 5485).

(5) Mac Farlane, D. R.; Meakin, P.; Sun, J.; Amini, N.; Forsyth, M. *J. Phys. Chem. B* **1999**, *103*, 4164.

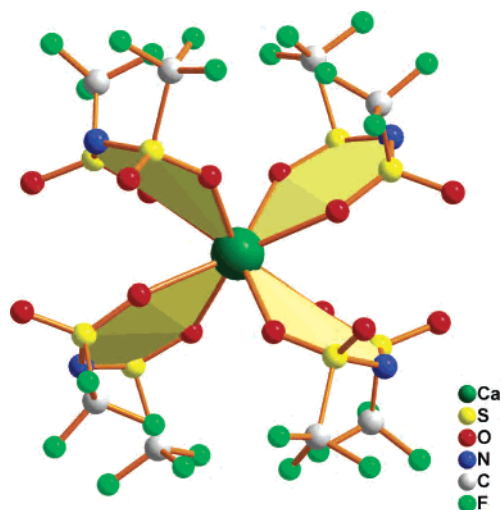


Figure 1. Coordination of Ca^{2+} by four Tf_2N^- ligands in the crystal structure of $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$.

$[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$: 108(s), 208(w), 231(w), 287(m), 329(m), 349(m), 411(w), 553(w), 571(w), 744(vs), 902(m), 1043(w), 1136(m), 1158(m), 1246(s), 1309(m), 1448(s) cm^{-1} .

3. Results and Discussion

Colorless, transparent crystals of the general composition $[\text{mppyr}]_2[\text{AE}(\text{Tf}_2\text{N})_4]$ for $\text{AE} = \text{Ca}$, Sr , or $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ are obtained from oversaturated solutions of the respective alkaline earth iodide in the ionic liquid $[\text{mppyr}][\text{Tf}_2\text{N}]$.

The calcium and strontium compounds crystallize in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. Both structures are not isotypic but homootypic, since the structures are similar but the fractional coordinates and the lattice constants are slightly different and the monoclinic angle is widened in $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ ($107.74(1)^\circ$ compared to $105.73(1)^\circ$ in $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$) (see Table 1). The asymmetric units of both crystal structures show the $\text{AE}(\text{II})$ -ions being coordinated by four Tf_2N^- anions forming a distorted square antiprism (see Figure 1 for $[\text{Ca}(\text{Tf}_2\text{N})_4]^{2-}$ and two cations of the ionic liquid to compensate the charge).

The $\text{Ca}-\text{O}$ distances range from 2.370(4) to 2.482(4) Å (cf. Table 2). With a mean $\text{Ca}-\text{O}$ distance of 2.41 Å, these are slightly shorter than the calcium–oxygen distance of oxygen atoms belonging to the bis(trifluoromethanesulfonyl)imide ligand in the hydrated calcium bis(trifluoromethanesulfonyl)imide, $\text{Ca}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})_2$ (2.466(4) and 2.502(4) Å).¹¹ This might be attributed to the fact that in the homoleptic compound $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ the Tf_2N^- ligands compete only with themselves, whereas in the hydrated calcium bis(trifluoromethanesulfonyl)imide, $\text{Ca}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})_2$, the weak Tf_2N ligand is forced to compete with the stronger coordinating oxygen donor atoms of the additional water molecules, leading to larger $\text{Ca}-\text{O}$ interatomic distances and, in turn, to a weaker $\text{Ca}-\text{O}$ bond whenever the Tf_2N ligand oxygen atoms are involved.

Because of the strong delocalization of the negative charge over all atomic centers and the high conformational flexibility

of the $\text{C}-\text{S}-\text{N}-\text{S}-\text{C}$ backbone, the Tf_2N ligand is regarded as a weakly coordinating anion (WCA).^{1,12} This is supported by the fact that, so far, for most known Tf_2N compounds the interatomic $\text{S}-\text{O}$ distances within the bis(trifluoromethanesulfonyl)imide anion are equal to or close to those in the free anion. This generally holds true for structures with “noncoordinating” cations.¹³ In contrast to this common observation, we find in $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ a rather significant elongation of the $\text{S}-\text{O}$ interatomic distances on the binding site of the ligands compared to the $\text{S}-\text{O}$ distances on the nonbinding site (1.447(4)–1.458(4) Å vs 1.421(4)–1.436(4) Å). This effect appears to be quite remarkable, especially since such a pronounced difference between the $\text{S}-\text{O}$ interatomic distances between the metal-bonded and unbound oxygen atoms is not observed in $\text{Ca}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})_2$.¹¹ This backs our hypothesis that the $\text{Ca}-\text{O}(\text{Tf}_2\text{N})$ bond is weakened in the presence of stronger coordinating ligands such as water, while in the pure presence of just bis(trifluoromethanesulfonyl)imide, calcium is forced to interact with the oxygen atoms belonging to the Tf_2N ligand. The same observation is made for the compounds $[\text{mppyr}]_2[\text{Ln}(\text{Tf}_2\text{N})_5]$ ($\text{Ln} = \text{Pr}$,¹⁴ Nd , or Tb) and $[\text{mppyr}]_2[\text{Ln}(\text{Tf}_2\text{N})_5]$ ($\text{Ln} = \text{Tm}$ or Lu)¹⁵ compared to $\text{La}(\text{Tf}_2\text{N})_3(\text{H}_2\text{O})_3$.¹¹

All Tf_2N^- ligands show a cisoid conformation with respect to the $-\text{CF}_3$ groups in $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ which pinches the $[\text{AE}(\text{Tf}_2\text{N})_4]^{2-}$ antiprisms along the crystallographic b -axis (Figure 2a). The $\text{S}-\text{N}$ interatomic distances ($d_{\text{mean}}(\text{N}-\text{S}) = 1.57$ Å) as well as the $\text{S}-\text{N}-\text{S}$ bonding angles ($\angle_{\text{mean}}(\text{S}-\text{N}-\text{S}) = 128^\circ$) are similar to the values found for the free ligand and in good agreement with theoretical calculations.⁴ The crystal structure of $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ is similar (though not isotypic) to the structure of $[\text{mppyr}]_2[\text{Yb}(\text{Tf}_2\text{N})_4]$,⁵ where the anionic parts are surrounded with the cation in a honeycomb-like lattice (Figure 2b).

In $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$, the $\text{Sr}-\text{O}$ distances range from 2.542(4) to 2.576(4) Å (see Table 2). With a mean value of 2.56 Å they are slightly smaller than in the “binary” $\text{Sr}(\text{Tf}_2\text{N})_2$ ($d(\text{S}-\text{O}) = 2.58$ Å). However, when we compare metal–oxygen distances of ligands which exhibit the same coordinating mode, for bidentately chelating Tf_2N ligands in $\text{Sr}(\text{Tf}_2\text{N})_2$ similar distances are found as in $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$, whereas $\text{S}-\text{O}$ distances involving bridging Tf_2N ligands seem to be generally larger. The influence of

(11) Xue, L.; DesMarteau, D. D.; Pennington, W. T. *Solid State Sci.* **2005**, *7*, 311.

(12) For overview on WCAs, see the following: (a) Krossing, I.; Raabe, I. *Angew. Chem.* **2004**, *116*, 2116–2142. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

(13) (a) Golding, J. J.; MacFarlane, D. R.; Spiccia, L.; Forsyth, M.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1998**, *15*, 1593. (b) Montanari, V.; DesMarteau, D. D.; Pennington, W. T. *J. Mol. Struct.* **2000**, *550/551*, 337. (c) Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. *Chem. Mater.* **2002**, *14*, 2103. (d) Schlueter, J. A.; Geiser, U.; Wang, H. H.; Kini, A. M.; Ward, B. H.; Parakka, J. P.; Daugherty, R. G.; Kelly, M. E.; Nixon, P. G.; Winter, R. W.; Gard, G. L.; Montgomery, L. K.; Koo, H.-J.; Whangbo, M.-H. *J. Solid State Chem.* **2002**, *168*, 524. (e) Davidson, M. G.; Raithby, P. R.; Johnson, A. L.; Bolton, P. D. *Eur. J. Inorg. Chem.* **2003**, 3445. (f) DesMarteau, D. D.; Pennington, W. T.; Montanari, V.; Thomas, B. H. *J. Fluorine Chem.* **2003**, *122*, 57. (g) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **2004**, 2267.

(14) Babai, A.; Mudring, A.-V. *Chem. Mater.* **2005**, *17*, 6230.

(15) Babai, A.; Mudring, A.-V. *J. Chem. Soc., Dalton Trans.*, in press.

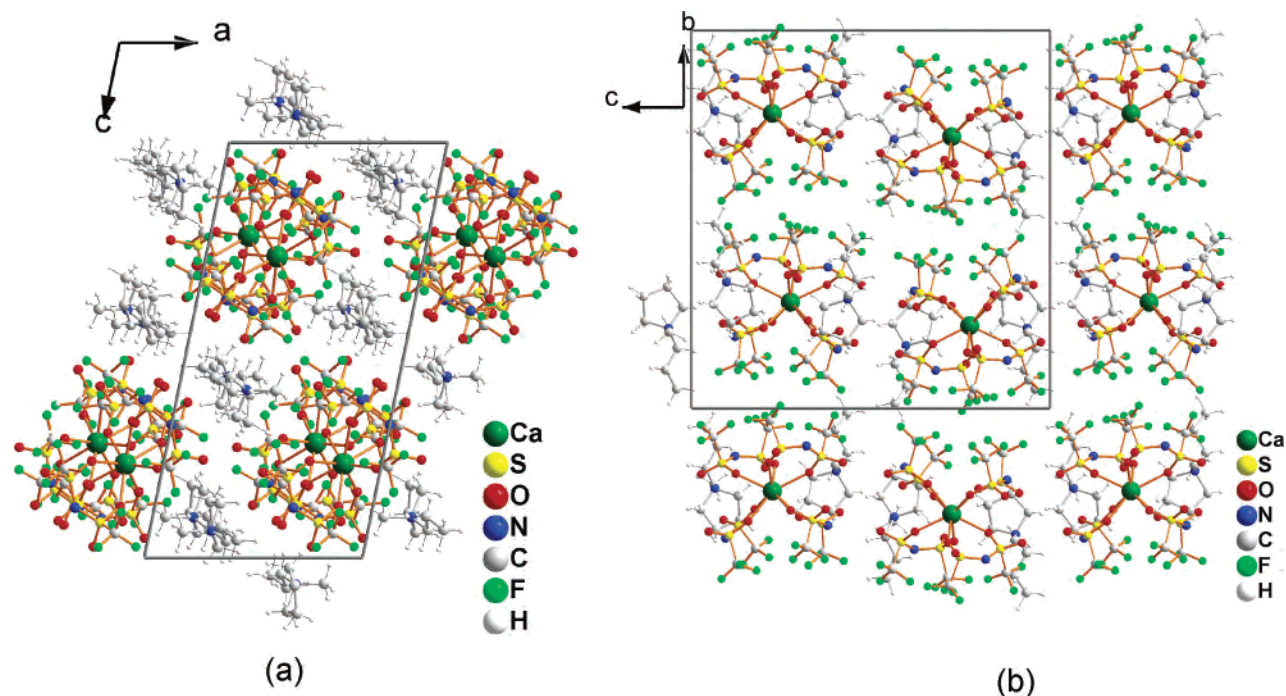


Figure 2. Projection of the crystal structure of $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ along the crystallographic (a) b - and (b) a -axes.

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

$[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$				$[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$				$[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$			
Ca–O1	2.370(4)	N1–S1	1.558(5)	Sr–O1	2.561(4)	N1–S1	1.549(5)	Ba1–O1	2.818(2)	N1–S1	1.574(2)
Ca–O2	2.384(4)	N1–S2	1.579(7)	Sr–O2	2.569(4)	N1–S2	1.559(7)	Ba1–O2	2.727(2)	N1–S2	1.574(2)
Ca–O3	2.391(4)	N2–S3	1.565(5)	Sr–O3	2.542(4)	N2–S3	1.555(5)	Ba1–O3	2.764(2)	N2–S3	1.565(2)
Ca–O4	2.405(3)	N2–S4	1.566(7)	Sr–O4	2.576(4)	N2–S4	1.563(7)	Ba1–O4	2.788(2)	N2–S4	1.578(2)
Ca–O5	2.427(4)	N3–S6	1.570(5)	Sr–O5	2.561(4)	N3–S6	1.543(7)	Ba1–O5	2.799(2)	N3–S5	1.566(3)
Ca–O6	2.446(4)	N3–S5	1.571(6)	Sr–O6	2.552(4)	N3–S5	1.565(9)	Ba1–O6	2.809(2)	N3–S6	1.577(3)
Ca–O7	2.468(4)	N4–S8	1.562(7)	Sr–O7	2.560(4)	N4–S7	1.554(7)	Ba1–O11	2.698(2)		
Ca–O8	2.482(4)	N4–S7	1.570(5)	Sr–O8	2.552(4)	N4–S8	1.558(6)	Ba1–O13	2.782(2)		
								Ba1–O15	2.746(2)		
S1–O1	1.451(4)	S1–N1–S2	128.4(3)	S1–O1	1.405(4)	S1–N1–S2	127.87(34)	S1–O1	1.434(2)	S1–N1–S2	126.72(16)
S1–O11	1.427(4)	S3–N2–S4	128.3(3)	S1–O11	1.392(6)	S3–N2–S4	127.49(34)	S1–O11	1.428(2)	S3–N2–S4	127.07(16)
S2–O2	1.458(4)	S6–N3–S5	127.2(3)	S2–O2	1.415(4)	S6–N3–S5	128.61(49)	S2–O2	1.429(2)	S5–N3–S6	125.81(17)
S2–O12	1.429(4)	S8–N4–S7	129.0(3)	S2–O12	1.431(6)	S7–N4–S8	127.99(40)	S2–O12	1.422(2)		
S3–O3	1.457(4)			S3–O3	1.405(4)			S3–O3	1.432(2)		
S3–O13	1.435(4)			S3–O13	1.415(6)			S3–O13	1.430(2)		
S4–O4	1.453(4)			S4–O4	1.411(4)			S4–O4	1.428(2)		
S4–O14	1.432(4)			S4–O14	1.406(5)			S4–O14	1.422(2)		
S5–O5	1.451(4)			S5–O5	1.427(4)			S5–O5	1.432(2)		
S5–O15	1.435(4)			S5–O15	1.408(6)			S5–O15	1.429(2)		
S6–O6	1.453(4)			S6–O6	1.422(4)			S6–O6	1.434(2)		
S6–O16	1.421(4)			S6–O16	1.454(9)			S6–O16	1.423(2)		

coordination on the S–O bond distance is far less pronounced than in the analogous calcium compound. As in $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$, in $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$ the N–S distances (1.56 Å) and S–N–S angles (128°) are unchanged upon coordination.

Because of the larger ionic radius of Sr^{2+} when compared to Ca^{2+} , the Sr–O distances in $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$ are significantly larger than the metal–oxygen distance in $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$. Thus, the propeller-like arrangement of the anions is widened in $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$ when compared to that in the Ca compound. In consequence, the heterocyclic cations have more space to order within the fluorine segregated layers which are stacked along the crystallographic a -axis (see Figure 3). In $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$

the cations are located in hydrophobic channels which are composed of the perfluoralkyl groups of the bis(trifluoromethanesulfonyl)imide ligands. The $\text{F}\cdots\text{H}\cdots\text{C}$ distances are too large ($d(\text{F}\cdots\text{H}\cdots\text{C}) \approx 2.6$ Å) for significant hydrogen-bonding.¹⁶ Furthermore, the cations, although they are clearly identified from the difference Fourier map, exhibit high displacement parameters after anisotropic refinement of the carbon skeleton even at low temperatures. This is taken as an indicator for weak interactions between the cationic and anionic parts of the structure.

In contrast to Ca^{2+} and Sr^{2+} which are coordinated by eight oxygen atoms of four Tf_2N^- ligands forming discrete anionic

(16) Steiner, T. *Angew. Chem.* **2002**, *114*, 50.

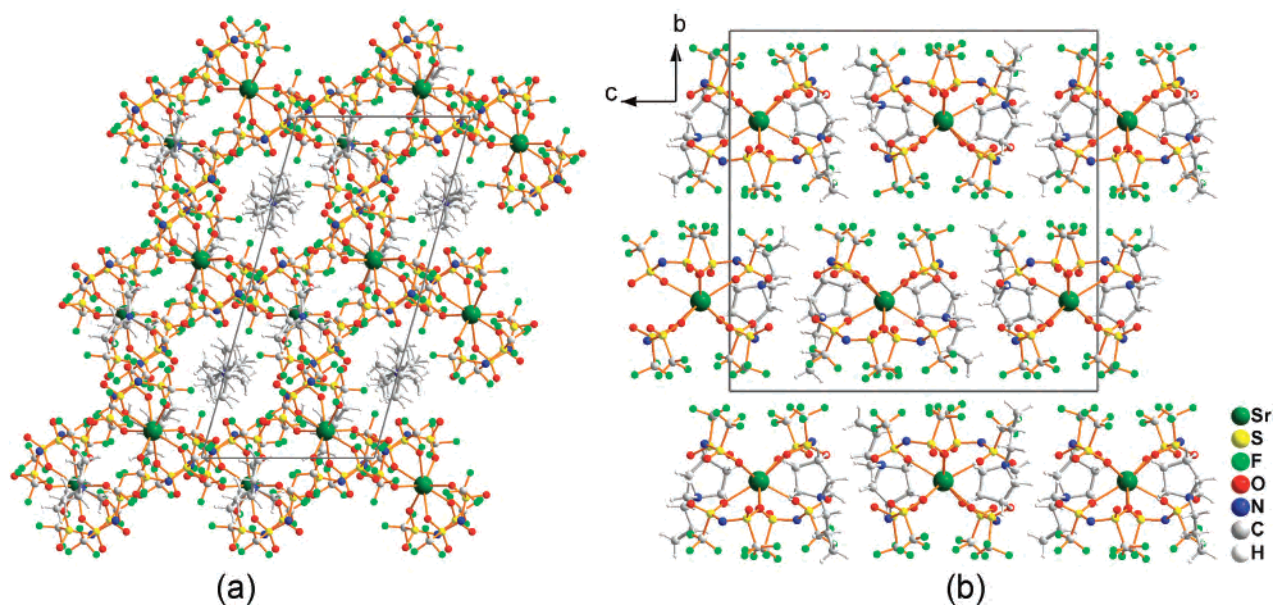


Figure 3. Projection of the crystal structure of $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$ along the crystallographic (a) *b*- and (b) *a*-axes.

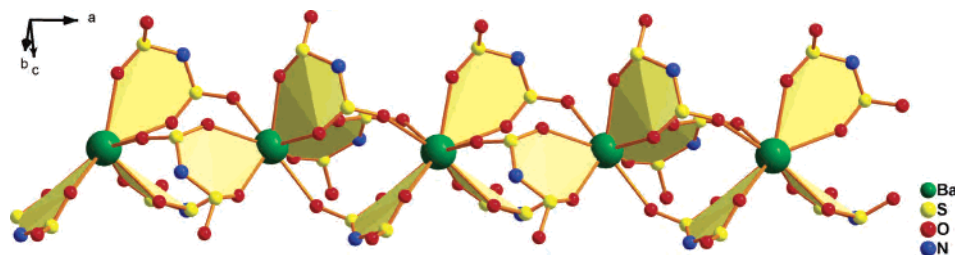


Figure 4. $\frac{1}{3}[\text{Ba}(\text{Tf}_2\text{N})_3]$ strands in $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ (fluorine atoms omitted for reasons of clarity).

moieties, the larger alkaline earth metal cation Ba^{2+} prefers a coordination number of 9. The barium–oxygen distances range from 2.698(2) to 2.818(2) Å with a mean value of 2.77 Å. This value is significantly less than the mean $\text{Ba}-\text{O}_{(\text{Tf}_2\text{N})}$ distance of 2.81 Å reported for $\text{Ba}(\text{H}_2\text{O})(\text{Tf}_2\text{N})_2$.¹¹ As previously pointed out for $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$ compared to $\text{Ca}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})_2$, this can be attributed to the fact that in $\text{Ba}(\text{H}_2\text{O})(\text{Tf}_2\text{N})_2$ the $\text{Ba}-\text{O}_{(\text{Tf}_2\text{N})}$ bond obviously gets weakened in the presence of coordinating water.

In $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$, the alkaline earth metal cation interacts with six oxygen atoms belonging to three Tf_2N^- anions which coordinate in a bidentately chelating mode and three further oxygen atoms which show monohapto ligand–metal interactions. The monohapto ligands are linking the Ba^{2+} cations to infinite chains along the *a*-axis (Figure 4).

These $\frac{1}{3}[\text{Ba}(\text{Tf}_2\text{N})_3]$ chains form a hexagonal arrangement (see Figure 5). The $[\text{mppyr}]$ cations are packed alongside the anionic chains in the crystal structure. The S–O interatomic distance within the bis(trifluoromethanesulfonyl)imide ligand gets lengthened slightly upon coordination (1.43 vs 1.42 Å), whereas the N–S (1.57 Å) and S–N–S angle (127°) virtually remain unchanged when compared to those of the free ligand. Again, all Tf_2N^- anions adopt a cisoid conformation.

It has been previously proposed that the Tf_2N^- anion would coordinate in a chelating mode through oxygen atoms

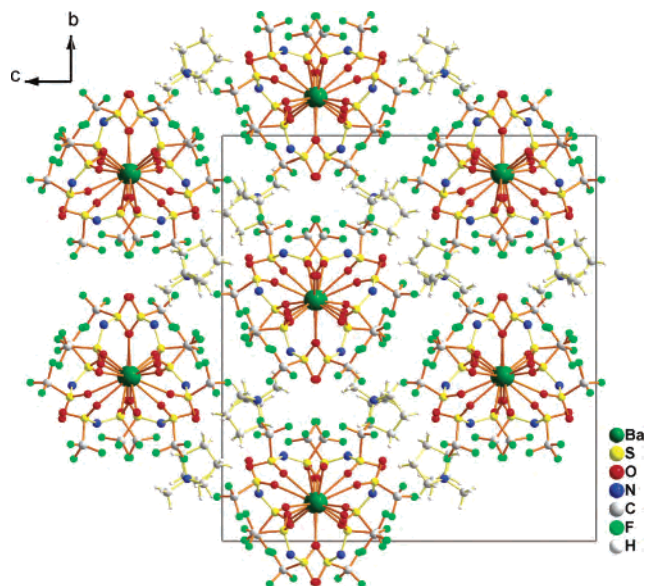


Figure 5. $\frac{1}{3}[\text{Ba}(\text{Tf}_2\text{N})_3]$ strands in $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$.

including nitrogen–metal interaction if the cation size is large enough as in the case of Ba^{2+} .¹⁷ Neither in $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ nor in $\text{Ba}(\text{H}_2\text{O})(\text{Tf}_2\text{N})_2$ is any nitrogen–metal

(17) Castriota, M.; Caruso, T.; Agostino, R. G.; Cazzanelli, E.; Henderson, W. A.; Passerini, S. *J. Phys. Chem. A* **2005**, *109*, 92.

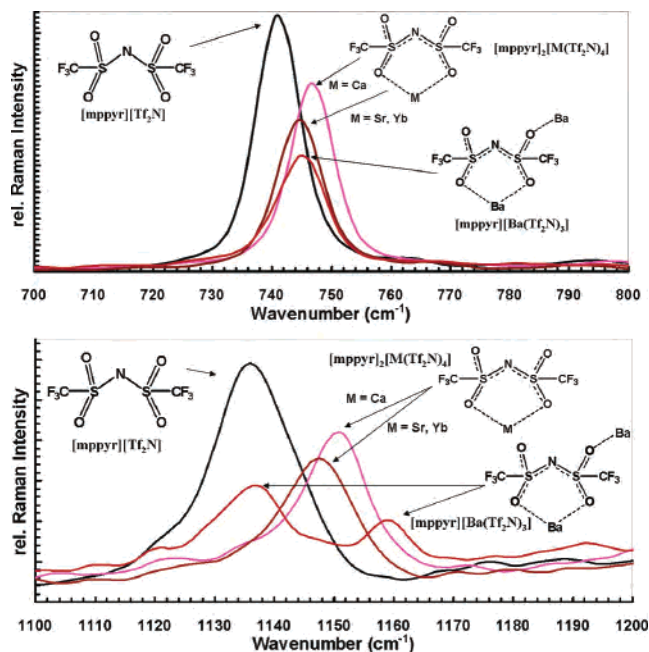


Figure 6. Raman spectra of $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$, $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$, and $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ in comparison with the ionic liquid $[\text{mppyr}][\text{Tf}_2\text{N}]$ itself.

interaction observed.¹⁸ This can be proven not only by the single-crystal X-ray structures but even better by Raman spectroscopic studies.

Raman Investigations. The characteristic Raman bands of the ionic liquid $[\text{mppyr}][\text{Tf}_2\text{N}]$ ¹⁷ as well as of the free acid HTf_2N ¹⁹ are well-known and have been assigned previously so that the coordination of the anion can be easily verified for bulk samples of the AE complexes.

The $\nu_s(\text{SNS})$ as well as the $\nu_s(\text{SO}_2)$ vibrations are the most relevant ones to study as they should be most influenced by interactions of the bis(trifluoromethanesulfonyl)imide with the metal cation. It has been claimed that upon deprotonation of HTf_2N the S–N bonds within the Tf_2N moiety are strengthened and gain partially a double bond character. Indeed, the expected shift of the $\nu_s(\text{SNS})$ band can be observed in the Raman spectra.¹⁹ For the “free” Tf_2N^- in the ionic liquid $[\text{mppyr}][\text{Tf}_2\text{N}]$ itself, the $\nu_s(\text{SNS})$ band is found at 740 cm^{-1} . Under complexation, the $\nu_s(\text{SNS})$ band of the anion shifts in the Ba and Sr complex to 744 cm^{-1} . The Ca complex shows the same shift to higher energy at 746 cm^{-1} (see Figure 6). In the free acid HTf_2N , the $\nu_s(\text{SNS})$ band is found around $\sim 770\text{ cm}^{-1}$.¹⁸ Thus, under complexation the frequency of the $\nu_s(\text{SNS})$ rises slightly when compared to that of the free anion.

The $\nu_s(\text{SO}_2)$ which should be directly influenced by coordination of the sulfonyl–oxygen to a metal center is observed for the free and quasi-noninteracting Tf_2N^- anion at 1136 cm^{-1} . In $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$, the band is located at 1149 cm^{-1} (see Figure 6). In the strontium compound, the band is shifted to 1145 cm^{-1} . Furthermore, for $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ the $\nu_s(\text{SO}_2)$ band is split into two peaks at 1136 and 1158 cm^{-1} . Hence, the position of the $\nu_s(\text{SO}_2)$ band is sensitive to both the mode of coordination and the coordinated metal itself. Apparently a stronger coordinative bond toward the metal center shifts the frequencies of the symmetric S–O stretching vibration to higher energy.

Judging from the Raman spectra, any contamination of the samples with $[\text{mppyr}][\text{I}]$, which is a byproduct of the reaction, can be excluded as none of the reported Raman frequencies of $[\text{mppyr}][\text{I}]$ could be detected.¹⁷

4. Conclusions

In the absence of any stronger competing ligands such as water, the homoleptic alkaline earth metal bis(trifluoromethanesulfonyl)imide complexes $[\text{mppyr}]_2[\text{Ca}(\text{Tf}_2\text{N})_4]$, $[\text{mppyr}]_2[\text{Sr}(\text{Tf}_2\text{N})_4]$, and $[\text{mppyr}][\text{Ba}(\text{Tf}_2\text{N})_3]$ were obtained from the respective alkaline earth metal iodide and the ionic liquid $[\text{mppyr}][\text{Tf}_2\text{N}]$. These compounds belong to the first examples of homoleptic alkaline earth metal bis(trifluoromethanesulfonyl)imides. Compared to the previously described water-containing alkaline earth metal bis(trifluoromethanesulfonyl)imides $[\text{Ca}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})_2]$ and $[\text{Ba}(\text{H}_2\text{O})_2(\text{Tf}_2\text{N})_2]$, a small but significant elongation of the sulfur–oxygen bond distance involving the coordinating oxygen is observed when compared to the free ligand. Furthermore, the interatomic EA–O(Tf_2N) distances are less in the homoleptic compounds than in the heteroleptic ones which may be indicative of a stronger metal–ligand interaction in the homoleptic compounds because of the absence of stronger donor ligands such as water. At the same time, upon coordination, the frequency of the symmetric S–O stretching vibration gets slightly shifted to larger values the stronger the metal is coordinating. The effect of complex formation on the S–N–S bonding angles and distances is negligible. The $\nu_s(\text{SNS})$ frequencies get slightly shifted to larger values upon complexation when compared to those of the free anion. Altogether these observations confirm once more that the bis(trifluoromethanesulfonyl)imide ligand can be regarded as comparatively weakly coordinating but by no means as noncoordinating! While chelating transoid structures are known,^{10,19} there appears to be a tendency that the Tf_2N anion prefers a cisoid conformation when coordinating in a chelating mode, whereas for the free anion the transoid conformation is strongly preferred (our calculations show the transoid structure of the free anion to be more stable by 4 kJ/mol compared to the cisoid one³). But structural data for Tf_2N complex compounds are still scarce to allow for a generalization. Common and typical for all structures now characterized is extensive fluorine segregation which results

(18) Note that a $\eta^2\text{-N}_2\text{O}$ coordination mode has been described for (cymene)–Ru(Tf_2N)₂: Williams, D. B.; Stoll, M. E.; Scott, B. L.; Costa, D. A.; Oldham, W. J. *Chem. Commun.* **2005**, 1438.

(19) (a) Foropoulos, J.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720. (b) Rey, I.; Johansson, P.; Lindgren, J.; Lassègues, J. C.; Grondin, J.; Servant, L. *J. Phys. Chem. A* **1998**, *102*, 3249.

(20) (a) Earle, M. J.; Hakala, U.; McAuley, B. J.; Nieuwenhuyzen, M.; Ramani, A.; Seddon, K. R. *Chem. Commun.* **2004**, 1368. (b) Xue, L.; Padgett, C. W.; DesMarteau, D. D.; Pennington, W. T. *Acta Crystallogr. C* **2004**, *60*, m200. (c) Xue, L.; Padgett, C. W.; DesMarteau, D. D. *J. Fluorine Chem.* **1991**, *52*, 7. (d) Nowinski, J. L.; Lightfoot, P.; Bruce, P. G. *J. Mater. Chem.* **1994**, *4*, 1579.

(21) Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Organometallics* **1999**, *18*, 3769.

Metal Bis(trifluoromethanesulfonyl)imide Complexes

in the formation of hydrophilic and hydrophobic structure parts.

Acknowledgment. The authors acknowledge the BMBF and Fonds der Chemischen Industrie for a Liebig fellowship to A.-V. Mudring, the Deutsche Forschungsgemeinschaft for

grants, and Prof. Dr. G. Meyer for his continuous support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC051820L