Polar Molecular Precursors for Alkali and Alkaline Earth Metal Clusters and Low-Dimensional Polymer Structures: the Solid-State Structures of [CaI(dme)$_3$]I, and *cis*-[SrI$_2$(diglyme)$_2$] (dme = CH$_3$OC$_2$H$_4$OCH$_3$; diglyme = CH$_3$(OC$_2$H$_4$)$_2$OCH$_3$)

Katharina M. Fromm*[a] and William Maudez[a]

Keywords: Alkaline earth metals / Calcium / Halides / Polar compounds / Strontium

Two new alkaline earth metal halide adducts with oxygen-donor polyether ligands are described. One of them, *cis*-[SrI$_2$(diglyme)$_2$], features two terminally bonded anions in vicinal positions, and at an angle of ca. 90°. The low bond valence sum of ca. 1.9 indicates how well the cation is shielded by its ligands in the solid state, and that ligand exchange can be expected in solution and upon reaction. The second compound, [CaI(dme)$_3$]I, consists of an ion pair formed by the cationic complex [CaI(dme)$_3$]$^+$ with one anion in terminal position, and one iodide. Both compounds possess a strong dipole moment at the molecular level, but crystallize in centrosymmetric space groups.

Introduction

We are interested in molecular compounds, especially oxygen donor adducts of alkaline earth metal iodides, because they are used as starting materials in the synthesis of low-dimensional polymeric compounds, including clusters.[1−10] The latter are used in the low-cost synthesis of superconductors and other oxide materials by the sol-gel technique, or as volatile precursors in CVD processes.[2,10] Furthermore, alkaline earth metal iodides complexed with polyether ligands have also been shown to have a dramatic effect on the dealkylation reactions of phosphinic esters.[11] We have also started to investigate the synthesis of polar materials for possible applications in NLO, for instance second harmonic generation. We became interested in these compounds because we wished to understand how they were formed and discover whether polar molecules can be forced to crystallize in polar space groups.

Compounds that have so far been isolated in the class of molecular species are, for instance, the zero-dimensional compounds *trans*-[CaI$_2$(THF)$_4$][12] or *trans*-[MI$_2$(THF)$_5$] (M = Sr,[13] Ba[1]), in which the metal cation is always surrounded in a linear or quasi-linear fashion by the two anions, whereas the THF ligands are found in the equatorial positions of a square or pentagonal bipyramid. They are commonly used as starting materials for substitution reactions of at least one iodide. Other compounds can also be molecular, but without any direct M−I contacts left to be reactive. Instead, the halide ions are replaced in the first coordination sphere by neutral water or polyether oxygen donor ligands for instance, leading to compounds such as [Ba(OH$_2$)(triglyme)$_2$]I$_2$ [triglyme = CH$_3$(OC$_2$H$_4$)$_3$OCH$_3$],[7] in which the anions are linked to the cationic complex by hydrogen bonding to the protons of the water molecules remaining in a second coordination sphere.

We now present some new exceptional molecular compounds that possess either two M−I bonds in *cis*-positions or only one M−I bond, leading in both cases to polar molecular precursors of alkaline earth metal iodides.

Results and Discussion

When SrI$_2$ is dissolved and re-crystallised from freshly dried and distilled diglyme (CH$_3$OC$_2$H$_4$OC$_2$H$_4$OCH$_3$), only the compound *cis*-[SrI$_2$(diglyme)$_2$] (**1**) is obtained. Compound **1** crystallises in the monoclinic space group $P2_1/c$ with two independent molecules A and B per asymmetric unit (Figure 1).[14] Both molecules consist of a strontium cation to which two diglyme ligands and two anions are directly linked, with Sr−I distances between 3.314(3) and 3.335(3) Å, the shorter bonds being found in the first molecule A with Sr1. They are 0.11 Å longer than the Sr−I bonds in other molecular strontium iodide adducts, firstly due to the higher coordination number in **1** (eight instead of seven), and secondly due to the intra-ionic repulsion between the iodides in the *cis*-positions.[10,13] On the other hand, they are shorter than the bonds in compounds where iodide plays the role of a μ-bridging ligand between two strontium cations.[10] The I1−Sr1−I2 angle is, at 91.26(9)°, slightly smaller than that in the second molecule,

---

[a] University of Karlsruhe, Institute for Inorganic Chemistry, Engesserstr., 76128 Karlsruhe, Germany
E-mail: katharina.fromm@chiam.unige.ch

DOI: 10.1002/ejic.200300241

I3−Sr2−I4 [91.78(9)°]. In addition to the anions, each alkaline earth metal cation is surrounded by two diglyme ligands, their oxygen atoms coordinating to the strontium ion with distances ranging between 2.614(7) and 2.731(8) Å. This results in a severely distorted square antiprismatic coordination sphere around the cation in each molecule. In molecule A, the bite angles of the diglyme ligand are 58.6(7)° and 60.8(7)° for the first, and 58.8(6)° and 60.6(6)° for the second ligand. In molecule B, the corresponding values are 61.1(7)°, 60.3(7)°, 60.7(6)° and 59.2(6)°, slightly larger than in molecule A. The O−Sr−O angles closest to linear are O1−Sr1−O6 [166.9(7)°] and O9−Sr2−O12 [165.6(7)°]. The other angles between the two diglyme ligands of each molecule are 74.3(6)° and 74.3(7)° for O1−Sr1−O4 and O3−Sr1−O6, respectively, and 80.9(3)° for O3−Sr1−O4 in molecule A, and 74.1(7)°, 74.3(7)° and 81.2(7)° for O9−Sr2−O10, O7−Sr2−O12 and O7−Sr2−O10, respectively, in molecule B. The C−O and C−C bonds are normal at 1.42 and 1.55 Å, respectively, on average, but with the general tendency of being slightly longer in molecule B than in molecule A. The molecules A and B can be considered as isolated as there aren't any close contacts between, for instance, the iodide of one molecule and hydrogen atoms of a neighbouring unit (>3 Å). Only one intramolecular H-bond can be found in molecule B, with a I3−H24B distance of 2.958(6) Å. There are no contacts between the iodides of one unit and the strontium cations of another, as the cation is completely protected by the organic ligands and its own anions. Thus, the shortest distance between the anions of one molecule and the cation of another is greater than 6 Å. Although there is some similarity between the two molecules A and B of **1**, no correlation matrix was found linking the two in order to indicate a higher symmetry. Furthermore, careful analysis of the X-ray data gave no hints for the presence of a higher symmetry. The relatively high *R* value is due to slight disorder in the polyether ligands as well as — and more importantly — to strong absorption effects, which could unfortunately not be corrected. This is not unusual for structures containing heavy elements such as iodine, and residual electron density as high as three electrons close to the anions in **1** has also been reported in other structures.[1]

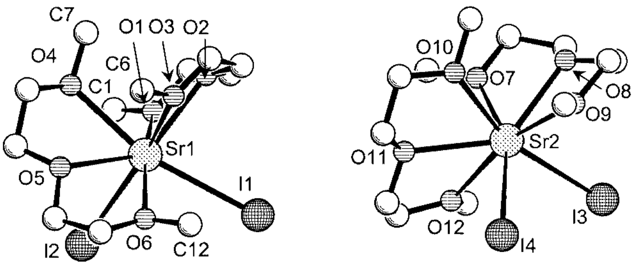

Figure 1. Two independent molecules of **1**; H atoms not shown

The coordination number of eight for the strontium cation is common. Generally, the strontium cation usually behaves more like barium than calcium as far as coordination numbers are concerned. Examples are found with a coordination number of seven in the compounds *trans*-[$\mathrm{MI_2(THF)_5}$] (M = Sr, Ba) whereas the corresponding calcium compound possesses a coordination number of six in *trans*-[$\mathrm{CaI_2(THF)_4}$], or for coordination number five as in [IM(O*t*Bu)$_4$(Li{thf})$_4$(OH)] for M = Sr and Ba, whereas the corresponding Ca compound has not been reported.[6,10] Barium compounds with sterically similar polyether ligands exist, and they all show a coordination number of nine for the alkaline earth metal cation, the corresponding bond valence sums being greater than two to satisfy the charge requirements.[7] In **1**, however, we observe a coordination number of eight for the strontium cation, and, more importantly, a bond valence sum of 1.95 and 1.91 for Sr1 and Sr2, respectively, which is obviously less than two.[15] This means that the cation is not sufficiently coordinated and would therefore be an excellent starting material for further synthesis, as it would tend to complete its coordination sphere by exchanging ligands for instance. However, the space-filling model of molecule A (Figure 2) shows how well the cation is shielded by its ligands, explaining why the bond valence sum remains below two.

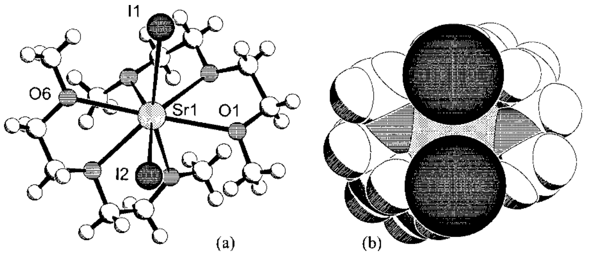

Figure 2. Molecule A of **1**: Sr1 and its coordination sphere as ball-and-stick model (a) and as space-filling representation (b)

The most intriguing fact about this structure is the fact that both anions occupy vicinal positions. This has never been observed before in a molecular species of the heavier alkaline earth metal halides, but only in two- or three-dimensional compounds with H-bonding involved,[5,7,16] or forming polymers or dimers with other anions of the neighbouring units.[1,17,18] For small alkaline earth metal cations, like Mg, with a coordination number of four, two anions are automatically in the vicinal positions, although with a larger angle between the anions than in **1**.[19] In general, to obtain such structures with the anions in *cis*-positions a sterically important ligand, which shields one side of the cation, such as slightly too small crown ethers, is required.[16] In these cases the X−M−X angles are usually much larger, the M−X bonds are longer than in **1**, and the anions are involved in H-bonding to build up a polymeric structure. Compound **1** is therefore the first example of a polar molecular alkaline earth metal iodide precursor. The strongly bent I−Sr−I feature in this structure is reminiscent of the alkaline earth metal halides, especially the heavier ones with strontium, barium and iodide as counterions, in the gas phase. Indeed, experimental as well as theoretical data show bent structures for the molecules in the gas phase.[20] So, **1** could be compared to a gas phase species stabilised by oxygen donor ligands. The bent structure is also reminiscent of the cyclopentadienyl derivatives of the alkaline earth metals. They have bent structures as well, although in the solid state they form polymers via contacts to neighbouring units. The THF-solvated cyclopentadienyl species are more similar to **1**.[21] More generally, other neutral complexes of alkaline earth metal cations, with coordination numbers greater than or equal to six, where two anions, such as halides or bulky amides for instance, are directly linked to the cation, preferentially show the anions organised in *trans*-positions. If the anions and further coordinating ligands are sterically more demanding, a distortion from the quasi-linear arrangement is observed, although it never reaches as small angles between the anions as in **1**.[17−19,22] Unfortunately, the polarity of the molecules of **1** is not maintained in the overall solid state as the compound crystallizes in a centrosymmetric space group.

The second compound presented here, $[CaI(dme)_3]I$ (**2**), was obtained by crystallizing CaI_2 from freshly dried and distilled DME.[14] It is built up from two independent cationic molecules A and B per asymmetric unit, each consisting of a calcium cation, Ca1 and Ca2, to which one iodide and three DME ligands are bonded terminally via both oxygen atoms, with two separate iodides as counterions (Figure 3). Thus, the cation reaches a coordination number of seven, that is, between six and eight, which are the most common coordination numbers for the calcium atom in general. The coordination geometry can roughly be described as a distorted pentagonal bipyramid with one iodide and an oxygen atom in axial positions. The corresponding I−Ca−O angle is, however, far from linear with an average value of 155°. This is due to the bite angles of the DME ligands, which vary from 63.7(4)° to 68.8(3)°. Of the five oxygen atoms in equatorial positions, one is clearly more out of the mean plane (formed by Ca and the five oxygen atoms) than the other four oxygen atoms, as has been described for a calcium compound with a similar coordination sphere.[9,23] The Ca−O bonds vary between 2.375(11) and 2.496(11) Å, the shorter bonds on average being found in molecule A around Ca1. The Ca−I bond is 3.120(3) Å and 3.121(3) Å for Ca1 and Ca2, respectively. This gives a cationic species for each molecule, the counterions I2 and I4 not being bonded at all to the cationic unit since all further Ca−I contacts are larger than 5.8 Å. In fact, there are no H−I contacts to I2 and I4 of less than 3.7 Å. Therefore, these anions can be considered as independent and not H-bonded to the cationic units. A similar compound can be obtained by replacing the three DME ligands of **2** by two, larger diglyme molecules. The number of oxygen atoms then remains identical, and so does their arrangement around the cation. The compound which is then obtained can be written as $[CaI(diglyme)_2]I$.[24] Unfortunately, crystals of both polar compounds are difficult to grow, as mentioned by Rogers et al.,[25] and the single crystal data is not yet of sufficient quality for publication. However, we have shown before that small polyether molecules (such as DME) can easily be replaced by larger ones (diglyme or triglyme for instance), as long as the number of oxygen atoms remains constant, without changes in the structure except for higher symmetries.[7]

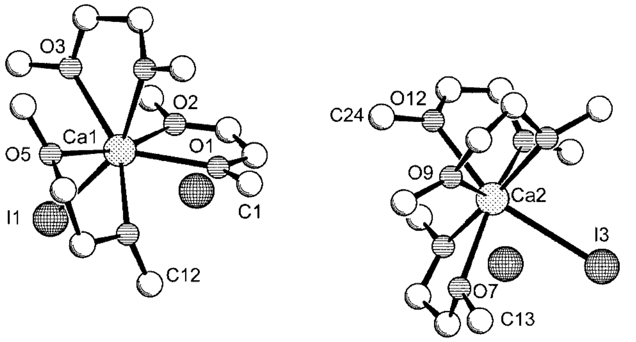

Figure 3. Two independent molecules of **2**; H atoms omitted for clarity

A heavier analogue to **2** with pseudo-halides is $[Sr(NO_3)(EO3)_2](NO_3)$ (EO3 = triethylene glycol)[25] where one anion is directly bonded to the cation whereas the other is weakly linked via H-bonds to an OH group of one of the polyglycols. In contrast to **2**, the H-bonding allows connections between anions and cationic units to form an overall threedimensional network. This is not observed in **2**.

The $[CaI(dme)_3]^+$ cations of **2** possess a strong dipole moment along the Ca−I bond vector, as can be seen from Figure 4. Such polar species are scarce: in the literature, only one example with calcium and iodide has been described so far to the best of our knowledge, $[CaI(THF)_5]^+$,[26] in which the cation possesses a coordination number of six, the counterion being an extremely bulky phosphonium diylide. The bond lengths in **2** are generally longer than in $[CaI(THF)_5]^+$, which is readily explained by the larger coordination number. In fact, the bond-valence sums for the calcium cations in **2** are, at 2.227 and 2.266, larger than the charge of the cation, indicating a more than satisfying bonding situation. The cation is indeed well wrapped up by its ligands, as shown in the space-filling model (Figure 4). Other polar compounds of alkaline earth metal cations linked to one halide and other neutral ligands can only be achieved when one coordination side of the cation is efficiently shielded by a sterically bulky ligand.[18,27] In some cases, formation of dimers occurs when

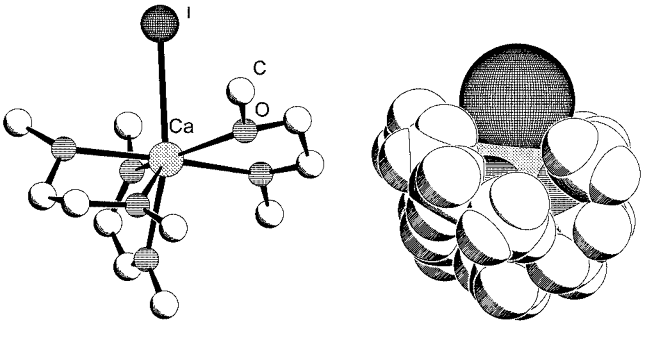

Figure 4. Cationic unit A $[CaI(dme)_3]^+$ of **2** and its space filling model

coordination sites on the cation remain empty, in order to avoid single polar units,[28,29] whereas other complexes form infinite polymer structures via H-bonding of the neutral ligands toward both of the linked and free anions.[24,30]

Conclusions

We have synthesised two adducts of alkaline earth metal halides, one of which carries both anions connected to the cation in mutual *cis*-positions, and the other with only one iodide bound to the cation with the second anion showing no interaction with the cationic units. Both compounds possess a strong dipole moment at the molecular level, although this vanishes in the overall solid-state structure as both crystallize in centrosymmetric space groups. Both type of species are rare in the chemistry of the heavier alkaline earth metal halides, and could therefore be useful alternatives for precursors in new substitution reactions as have been described in the literature on *trans*-alkaline earth metal iodide adducts.[10,12,13,17] In all of the examples cited above, the polarity remains a local phenomenon, whereas the compounds crystallize in centrosymmetric space groups, so that the dipole moment vanishes in the solid state. We are now investigating the possibilities of crystallizing these compounds, **1** and **2**, in polar space groups, relying on the presence of polar ion pairs in solution.

Experimental Section

General: All experiments were carried out under an inert nitrogen atmosphere, using Schlenk techniques. The solvents DME and diglyme (diethylene glycol dimethyl ether) were dried over Na/benzophenone and distilled under nitrogen prior to use. IR spectra were carried out on a Perkin−Elmer Spectrum One IR spectrometer.

1: SrI_2 (0.174 g, 0.51 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 30 mL of freshly dried and distilled diglyme, heating to reflux. The solution was filtered while hot and was then left to stand at room temperature. After two days, colourless single crystals grow in a yield of 78% with respect to SrI_2. $C_{24}H_{56}I_4O_{12}Sr_2$ (1219.6): calcd C 23.64, H 4.63; found C 25.97, H 5.27. The differences between found and calculated values are due to solvent, which remains on the crystals as they can't be dried under vacuum, and decompose rapidly if left in air. IR (nujol, CsI plates): $\tilde{\nu}$ = 2849 cm^{-1} (Nujol), 2077(w), 1971(w), 1939(w), 1605, 1459(Nujol), 1380(m), 1354(Nujol), 1286(m), 1269(w), 1249(vs), 1203(vs), 1129(s, sh), 944(m), 870(s), 839(s), 723(Nujol), 559(s), 489(w), 461(m), 367(w)

2: CaI_2 (0.24 g, 0.817 mmol) was dried under vacuum for half an hour at 300 °C, and then dissolved in 30 mL of freshly dried and distilled DME by heating to reflux for 15 minutes. The solution was filtered while hot, and colourless single crystals of **2** formed within one day at room temperature. Out of the mother liquor, crystals quickly lose solvent, as can be observed under the microscope, where they turn from clear colourless to opaque. The yield has therefore been estimated at 70% with reference to CaI_2. The lower evaporation temperature of DME compared to diglyme explains the values found for elemental analysis, where values are generally too low. $C_{24}H_{60}Ca_2I_4O_{12}$ (1128.5): calcd. C 25.54, H 5.36; found C 21.47, H 4.9. IR (nujol, CsI plates): $\tilde{\nu}$ = 863 cm^{-1} (Nujol), 2059(w), 1915(w), 1622(m), 1465(Nujol), 1374(Nujol), 1285(s), 1247(s), 1192(s), 1123(w, sh), 937(w), 859(vs), 721(Nujol), 569(m), 387(s)

[1] K. M. Fromm, *Angew. Chem.* **1997**, *109*, 2876−2878; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2799−2801.

[2] K. M. Fromm, *Chem. Commun.* **1999**, *17*, 1659−1660.

[3] K. M. Fromm, G. Bernardinelli, H. Goesmann, M.-J. Mayor-Lopez, J. Weber, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1685−1691.

[4] K. M. Fromm, G. Bernardinelli, H. Goesmann, *Polyhedron* **2000**, *19*, 1783−1789.

[5] K. M. Fromm, H. Goesmann, *Acta Crystallogr., Sect. C* **2000**, *56*, 1179−1180.

[6] K. M. Fromm, E. D. Gueneau, H. Goesmann, *Chem. Commun.* **2000**, 2187−2188.

[7] K. M. Fromm, *Chem. Eur. J.* **2001**, *7*, 2236−2244.

[8] K. M. Fromm, G. Bernardinelli, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1626−1630.

[9] K. M. Fromm, *Cryst. Eng. Commun.* **2002**, *4*, 318−322.

[10] K. M. Fromm, E. D. Gueneau, G. Bernardinelli, H. Goesmann, J. Weber, M.-J. Mayor-López, P. Boulet, H. Chermette, *J. Am. Chem. Soc.* **2003**, *125*, 3593−3604.

[11] D. Albanese, D. Landini, A. Maia, *J. Org. Chem.* **2001**, *66*, 3249−3252.

[12] K. F. Tesh, D. J. Burkey, T. P. Hanusa, *J. Am. Chem. Soc.* **1994**, *116*, 2409−17.

[13] K. Ruhlandt-Senge, K. Davis, S. Dalal, U. Englich, M. O. Senge, *Inorg. Chem.* **1995**, *34*, 2587−92; K. M. Fromm, unpublished results.

[14] **Structural Data for 1**: $C_{24}H_{56}I_4O_{12}Sr_2$, M = 1219.52 g·mol^{-1}, monoclinic, space group $P2_1/c$, a = 19.723(4), b = 15.262(3), c = 14.066(3) Å, β = 90.50(3)°, V = 4233.9(2)Å^3, Z = 4, $\rho_{calcd.}$ = 1.913 Mg·m^3, $F(000)$ = 2336, T = 203 K, λ = 0.71069 Å, μ(Mo-K_α) = 5.482 mm^{-1}, $3.38° < 2\theta < 45.08°$, 5539 reflections of which 5539 unique and 5304 observed, 388 parameters refined, *GOOF* (on F^2) = 1.010, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.1119$, $wR2 = 0.2749$ for $I > 2\sigma(I)$ and $R1 = 0.1701$, $wR2 = 0.3213$ for all data.
Structural Data for 2: $C_{24}H_{60}Ca_2I_4O_{12}$, M = 1128.48 g·mol^{-1}, monoclinic, space group $P2_1/n$, a = 13.594(3), b = 17.256(4), c = 18.638(4) Å, β = 91.91(3)°, V = 4369.6(15)Å^3, Z = 4, $\rho_{calcd.}$ = 1.715 Mg·m^3, $F(000)$ = 2208, T = 203 K, λ = 0.71069 Å, μ(Mo-K_α) = 3.131 mm^{-1}, $3.22° < 2\theta < 50.16°$, 14562 reflections of which 7691 unique, 392 parameters refined, *GOOF* (on F^2) = 1.813, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.1217$, $wR2 = 0.3208$ for $I > 2\sigma(I)$ and $R1 = 0.2172$, $wR2 = 0.3908$ for all data.
Crystal data for **1** and **2** were measured on a STOE CAD-4 diffractometer equipped with monochromated graphite Mo-K_α radiation (λ = 0.71073 Å) and an Oxford Cryosystems open flow cryostat.[31] No absorption correction was possible due to decomposition of the crystals during measurement. The structures were solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-99 package.[32] All heavy atoms could be refined anisotropically. Disorder was observed for the ethyl groups of the polyether ligands in **1** and **2**. CCDC-206570 (**1**) and -206569 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

[15] M. O'Keeffe, N. E. Brese, *J. Am. Chem. Soc.* **1991**, *113*, 3226−3229. G. J. Palenik, *Inorg. Chem.* **1997**, *36*, 122.

[16] P. C. Junk, L. M. Louis, M. K. Smith, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1196−1209.

[17] M. J. Harvey, T. P. Hanusa, *Organomet.* **2000**, *19*, 1556–1566.
[18] B. W. Skelton, A. F. Waters, A. H. White, *Austr. J. Chem.* **1996**, *49*, 99–115.
[19] A. F. Waters, A. H. White, *Aust. J. Chem.* **1996**, *49*, 35–46.
[20] M. Kaupp, P. v. R. Schleyer, H. Stoll, H. Preuss, *J. Am. Chem. Soc.* **1991**, *113*, 6012–6020; M. Kaupp, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1993**, *115*, 11202–11208 and references cited therein.
[21] R. Zerger, G. Stucky, *J. Organomet. Chem.* **1974**, *80*, 7–17. M. J. Mc Cormick, R. A. Williams, L. J. Levine, T. P. Hanusa, *Polyhedron* **1988**, *7*, 725–730. M. Westerhausen, C. Gückel, H. Pietrowski, P. Mayer, M. Warchhold, H. Nöth, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1741–1750.
[22] M. Westerhausen, *Coord. Chem. Rev.* **1998**, 157–210. M. Westerhausen, S. Weinrich, M. Ossberger, N. W. Mitzel, *Z. Anorg. Allg. Chem.* **2003**, *629*, 575–577 and references cited therein.
[23] K. M. Fromm, *Chimia* **2002**, *56*, 676–680.
[24] K. M. Fromm, W. Maudez, unpublished results.
[25] R. D. Rogers, M. J. Jezl, C. B. Bauer, *Inorg. Chem.* **1994**, *33*, 5682–5692.
[26] E. D. Brady, T. P. Hanusa, M. Pink, V. G. Young, Jr., *Inorg. Chem.* **2000**, *39*, 6028–6037.
[27] D. Fenske, G. Baum, H. Wolkers, B. Schreiner, F. Weller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1993**, *619*, 489–499. A. N. Chekhlov, *Russ. J. Coord. Chem.* **2001**, *27*, 381–386.
[28] Y. Yokota, R. A. Jacobson, B. C. Logsdon, S. Ringrose, A. T. Setterdahl, J. G. Verkade, *Polyhedron* **1999**, *18*, 2519–2532.
[29] A. F. Waters, A. H. White, *Aust. J. Chem.* **1996**, *49*, 147–154, and therein.
[30] A. F. Waters, A. H. White, *Aust. J. Chem.* **1996**, *49*, 61–72.
[31] J. Cosier, A. M. Glazer, *J. Appl. Crystallogr.* **1986**, *19*, 105.
[32] G. M. Sheldrick, SHELX-99, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, **1999**.

Received April 28, 2003