Alkaline-Earth-Metal Complexes

Linear Finite "Mers"—Homoleptic Polynuclear Heavy Alkaline Earth Metal Pyrazolates**

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The increased demand for highly volatile precursor molecules for the production of Group 2 solid-state materials sparked our interest in alkaline earth metal pyrazolate (pz) chemistry. Well explored for di- and trivalent rare earth metal derivatives,[1,2] the pyrazolate ligand system is uniquely capable to induce a multitude of metal–ligand binding modes.[2,3] This structural flexibility, when used in conjunction with donor molecules, enabled the isolation of several families of monomeric alkaline earth metal pyrazolates.[4,5] Studies probing the utility of the pyrazolates as precursor molecules showed that not all compounds sublime intact,[5,6] and frequently loss of donors and consequent reduction in volatility is observed. As an example, Winter and co-workers reported that $[Ca(tBu_2pz)_2(thf)_2]$ (tBu_2pz = 3,5-di-*tert*-butylpyrazolate; thf = tetrahydrofuran) sublimes with partial decomposition (200 °C, 0.1 mm Hg) into a white solid of the composition $[Ca(tBu_2pz)_2]_n$ but with an unknown structure.[5]

Herein we present a family of coligand-free, heavy alkaline earth metal pyrazolates, rare examples of homoleptic linear oligomers with a noteworthy array of metal–ligand binding modes. These feature a metal-size dependent degree of association, namely, the trimeric $[Ca_3(tBu_2pz)_6]$ **1**, the tetrameric $[Sr_4(tBu_2pz)_8]$ **2** and the unprecedented hexameric $[Ba_6(tBu_2pz)_{12}]$ **3**. The only other structurally characterized homoleptic alkaline earth metal pyrazolate is the dimeric $[Mg_2(tBu_2pz)_4]$ **4**,[3g] which is now shown to be the junior member of the series.

Compounds **1**–**3** were prepared by the direct treatment of 3,5-di-*tert*-butylpyrazole (tBu_2pzH) with the appropriate metal at 250 °C [Eq(1)]. X-ray quality crystals were obtained by recrystallization from a nondonating high-boiling solvent or sublimation.

$$n\,M + 2n\,tBu_2pzH \rightarrow [M_n(tBu_2pz)_{2n}]\ (\mathbf{1}-\mathbf{3})\ + n\,H_2$$
$$\mathbf{1}:\ M = Ca,\ n = 3;\ \mathbf{2}:\ M = Sr,\ n = 4;\ \mathbf{3}:\ M = Ba,\ n = 6 \qquad (1)$$

The solid-state structures of **1**–**3** were established by low temperature X-ray crystallography.[7] The structures of compounds **1**–**3** are presented in Figures 1–3, showing linear chains held together by diverse types of bridging pyrazolates.

Plausibly, $[Ca_3(tBu_2pz)_6]$ **1** corresponds to the product of thermal decomposition of $[Ca(tBu_2pz)_2(thf)_2]$,[5] as mentioned above. Thus, important information is obtained on the fate of the monomeric solid-state precursors upon solvent loss as frequently experienced in a CVD reactor. Complex **1** displays

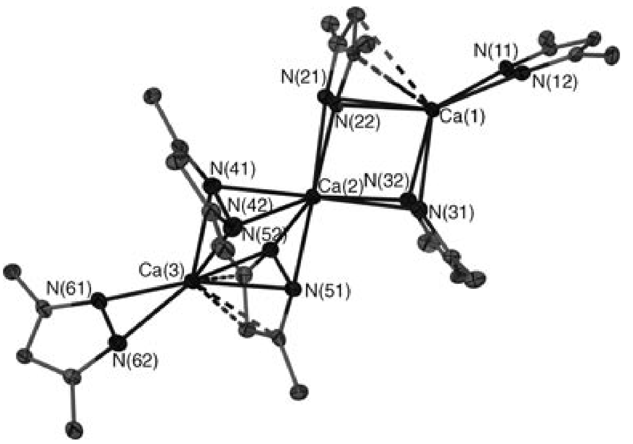

Figure 1. Structure of $[Ca_3(tBu_2pz)_6]$ **1**; *tert*-butyl groups have been omitted for clarity. (Ca(1)-N(11,12,21,22,31,32) 2.303(3), 2.318(3), 2.577(3), 2.583(3), 2.447(4), 2.450(4), Ca(1)-C(23, 24, 25) 2.816(5)-2.960(4) Å;, Ca(2)-N(21,22,31,32,41,42,51,52) 2.446(3), 2.418(3), 2.557(4), 2.597(4), 2.517(4), 2.618(4), 2.455(4), 2.415(4) Å; Ca(3)-N(41,42,51,52,61,62) 2.481(4) Å, 2.438(4), 2.560(4), 2.610(3), 2.292(3), 2.327(3) Å; Ca(3)-C(53,54,55) 2.804(4)-2.995(4) Å).

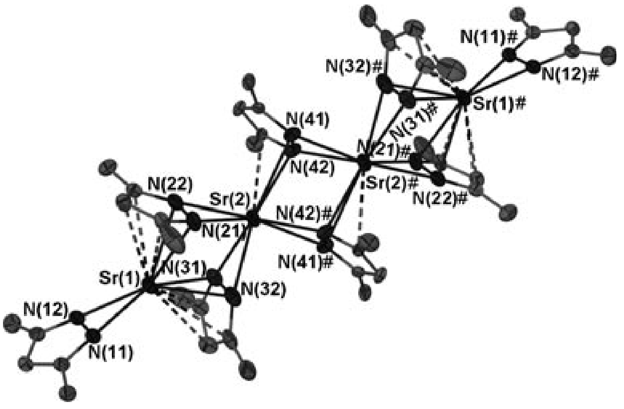

Figure 2. Structure of $[Sr_4(tBu_2pz)_8]$ **2**; *tert*-butyl groups and the disordered components pzX, pzY, pz5 have been omitted for clarity. (Sr(1)-N(11,12,21,22,31,32) 2.485(5), 2.455(5), 2.758(7), 2.730(6), 2.779(6), 2.741(7) Å; Sr(1)-C(23,24,25,33,34,35) 3.029(7)-3.381(9) Å; Sr(2)-N(21,22,31,32,41,42,41#,42#) 2.586(7), 2.575(7), 2.648(6), 2.580(8), 2.913(9), 2.734(9), 2.453(9), 2.523(9) Å; Sr(2)-C(43) 3.22 (1) Å).

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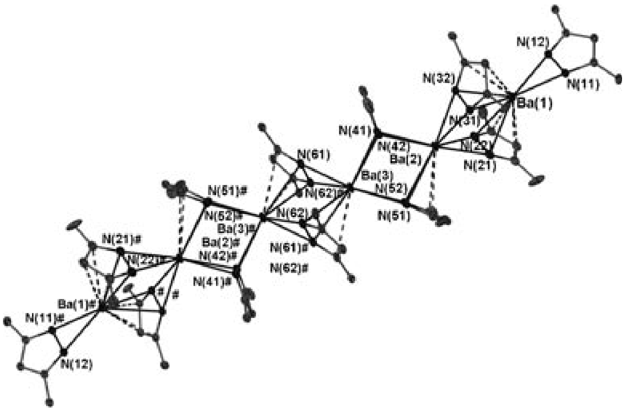

Figure 3. Structure of $[Ba_6(tBu_2pz)_{12}]$ **3**; *tert*-butyl groups and the disordered components pz2′, pz3′, pz4′, pz5′ and pz6′ have been omitted for clarity. (Ba(1)-N(11,12,21,22,31,32) 2.610(7), 2.651(7), 2.96(1), 2.96(1), 2.90(1), 2.89(1), Ba(1)-C(23,24,25,33,34,35) 3.10(1)-3.39(1) Å; Ba(2)-N(21,22,31,32,41,42,51,52) 2.84(1), 2.83(1), 2.72(1), 2.79(1), 2.79(1), 2.77(1), 2.98(1), 3.06(1) Å, Ba(2)-C(53,55) 3.38(2), 3.28(2) Å; Ba(3)-N(41,42,51,52,61,62) 2.92(1), 2.85(1), 2.69(1), 2.78(1), 2.67(1), 2.59(1) Å; Ba(3)#-N(61,62) 3.06(1), 3.08(1) Å; Ba(3)#-C(63,65) 3.36(1), 3.33(1) Å).

a linear array of calcium atoms, linked by pyrazolate bridges, and framed by two terminally bonded symmetrical ($Ca-N_{ter}$ 2.292(3)–2.327(3) Å) η^2-pyrazolates, which are in line (pz1 165.2(1)°, pz6 167.0(1)°) with the Ca(1)-Ca(3) axis. There are two classes of bridging pyrazolates: pz3 and pz4 that display μ-η^2:η^2 coordination with ligand planes perpendicular to the Ca_3-axis (pz3 85.7(1)°, pz4 86.1(1)°), while pz2 and pz5 are inclined towards the outer calcium atoms (pz2 36.4(1)°, pz5 41.9(1)°). The resulting close proximity of calcium to the carbon atoms of the pyrazolate rings pz2 and pz5 (Ca–C 2.804(4)–2.995(4) Å) reveals distances that lie well within the sum (3.7 Å) of the metallic radius of Ca (1.97 Å)[8] and the van der Waals radius of an aromatic ring (1.73 Å),[9] thus suggesting μ-η^2:η^5 ligation of calcium. Both bonding modes contrast the more common μ-η^1:η^1 bridging observed in $[Mg_2(tBu_2pz)_4]$.[3g] When the overall coordination number is taken into account, these distances compare well with the Ca π–arene interactions in sandwich complexes such as $[Ca(Cp)_2]_n$ or $[Ca(Cp^*)_2]$.[10] Surprisingly, there is a higher formal coordination number (8) for the central metal than for the outer metals (7) but the points of attachment ($\Sigma\eta^n = 9$) for Ca(1,3) exceed that (8) for Ca(2). The pairs of μ-η^2:η^2 and μ-η^2:η^5 bridges resemble the structures of $[Ln_3(Ph_2pz)_9]$ (Ln = La, Nd; Ph_2pz = 3,5-diphenylpyrazolate).[11]

The tetranuclear complex **2** is a dimer of dinuclear units. The terminal pyrazolates bind fairly symmetrically ($Sr-N_{ter}$ 2.455(5), 2.485(5) Å) and are parallel to the Sr_4 axis (pz1 172.3(2)°); but in contrast to the calcium analogue all bridging pyrazolates are now inclined. Nevertheless, the degree of tilting varies leaving only the outer pyrazolates at an almost ideal angle for π-bonding (pz2 43.5(3)°, pz3 41.1(4)°; Sr(1)-N_{br} 2.730(6)–2.779(6) Å) and μ-η^2:η^5-bridging. The larger inclination angle of the central pz4 ring towards Sr(2) (48.4(3)°) allows close contacts only for C(43) (Sr-C 3.22(1) Å), hence displaying a μ-η^2:η^3 metal coordination, previously known only in lanthanoid coordination.[3c,d] The corresponding europium complex $[Eu_4(tBu_2pz)_8]$ **5**[2c] is isomorphous with **2**, the only minor structural difference consisting of a slightly smaller inclination angle (46.6(7)°) towards the central metals.

The hexanuclear barium complex **3** is a dimer of trinuclear units with three different types of barium centers. Analogous to **1** and **2**, the terminal metals are sandwiched between two μ-η^2:η^5-pyrazolates (pz2 45.6(6)°, pz3 47.2(5)°) and a terminal η^2-pyrazolate (Figure 3). While Ba(1) and Ba(2) are bridged by two μ-η^2:η^5-pyrazolates, Ba(2) and Ba(3) are connected by a μ-η^2:η^2- (pz4 87.8(9)°) and an inclined (towards Ba(2)) μ-η^2:η^4-pyrazolate (pz5 44.8(8)°). The central bridging pyrazolate pz6/pz6′ (′ indicates disordered components) between Ba(3) and Ba(3)# is tilted 44.7(9)° towards the symmetry generated metal ($Ba(3)-N_{br}$ 2.421(9)–2.67(1) Å; $Ba(3)\#-N_{br}$ 3.054(9)–3.203(9) Å). Surprisingly, pz6′ shows the most unsymmetrical bridging with even shorter (0.18 Å) Ba(3)–N contacts than the terminal η^2-pyrazolate pz1 and even more elongated Ba(3)#–N(61′) (3.203(9) Å) bonds than the other μ-η^2:η^4-pyrazolates. Overall, the barium–pyrazolate interactions (Figure 3) compare well with those of $[Ba_6(Me_2pz)_8(thf)_6\{(OSiMe_2)_2O\}_2]$ **6**,[12] which has terminal η^2-Ba-N 2.665(9), 2.694(8) Å; μ-η^2:η^2-Ba-N 2.792(7)–3.007(8) Å ; and μ-η^2:η^5-Ba-N 2.755(7)–2.984(8) Å.

A low-temperature ^1H NMR spectrum in $[D_8]$toluene of **2** shows the separation of the pz(C4–H) signal into three well defined peaks with a ratio of 2:2:4 upon cooling to −60 °C, which correspond to the three different ligand-binding types, thus confirming the geometrical arrangement observed in the solid state. The corresponding spectrum of **1** shows the same trend but incomplete separation of the three signals negates integration. The broad *tert*-butyl signal at room temperature changed into overlapping singlets at low temperature for both compounds. Insufficient solubility of **3** precluded analogous studies. Instead, the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **3** in $[D_8]$THF revealed sharp peaks that correspond to a single magnetic environment consistent with the formation of a solvated, monomeric complex. However, extraction of crude **1**–**3** with THF and crystallization yield dimeric $[\{M(tBu_2pz)_2(thf)_n\}_2]$, which are being structurally characterized.[13]

Isolation of **1**–**3** together with the earlier **4** shows that in the series $[\{M(tBu_2pz)_2\}_n]$, the degree of association increases with the ionic radius of the metal with $n = 2$ (Mg),[3g] 3 (Ca), 4 (Sr), 6 (Ba). Although this is not associated with a major change in formal coordination number, except from Mg (CN = 4) to Ca (CN = 7,8), the points of attachment increase on descending the group, from **1** ($\Sigma\eta^n = 9$ Ca(1,3), 8 Ca(2)) to **2** ($\Sigma\eta^n = 12$ Sr(1), 9 Sr(2)) and **3** ($\Sigma\eta^n = 12$ Ba(1), 10 Ba(2,3)), thus supporting the lengthening of the chain.

The stable trinuclear **1** is in striking contrast to the behavior of ytterbium (ionic radii of Yb^{2+} and Ca^{2+} are comparable)[14] for which direct metallation between tBu_2pzH and excess metal affords the mixed oxidation state species $[Yb_2^{II,III}(tBu_2pz)_5]$.[15] On the other hand, with **2** being isomorphous with **5**, the close relationship between alkaline earth and rare earth metals (in this case Sr^{2+}/Eu^{2+}) is reinforced. There are even similarities between calcium and trivalent rare earth derivatives, shown by a comparison of **1** with $[Ln_3(Ph_2pz)_9]$ (Ln = La, Nd).[11] They both have μ-η^2:η^2 and μ-η^2:η^5 bridging and a lower formal coordination number for the terminal metal, despite the difference in the metal framework (**1** linear/$[Ln_3(Ph_2pz)_9]$ bent).

Experimental Section

The compounds described herein are extremely air- and moisture-sensitive and so require all manipulations to be carried out under an inert-gas atmosphere. 3,5-Di-*tert*-butylpyrazole[16] (0.72 g, 4.0 mmol), excess alkaline earth metal pieces (Ca, 0.41 g; Sr, 0.88 g; Ba, 1.37 g; 10 mmol), and 1,2,4,5-tetramethylbenzene (≈0.5 g) were heated in a sealed, evacuated Carius tube at 250 °C for 48 h. After sublimation of the solvent, the excess metal pieces were removed and the crude product washed with hexane (30 mL) leaving a white solid of good purity. Crystals suitable for X-ray diffraction were obtained by recrystallisation of small amounts of product from 1,2,4,5-tetramethylbenzene for **1** and **2** and 1,3,5-tri-*tert*-butylbenzene for **3**. Pure material was also obtained by sublimation, but the mechanical stress on the crystals upon removal from the walls of the reactor decreased crystal quality. Crystallographic analyses for compounds **1**–**3** were conducted as described.[4a] The bridging pyrazolates in **2** and **3** are disordered over two sites (**2**: occupancy pz2,pz3/pzX,pzY 0.82/0.18; pz4/pz5 0.56/0.44; **3**: pz2/pz2′ 0.65/0.35; pz3/pz3′ 0.63/0.37; pz4/pz4′ 0.52/0.48; pz5/pz5′ 0.55/0.45; pz6/pz6′ 0.61/0.39) in addition to disorder due to the rotation of the *tert*-butyl groups. IR data for **2** and **3** and ^{13}C NMR for **1**–**3** are listed in the Supporting Information.

1: $[Ca_3(tBu_2pz)_6]$ (0.76 g, 95 %). M.p. (sealed tube/N_2): 168–173 °C; IR (Nujol): $\tilde{\nu} = 3108$ (m), 2713 (m), 2196 (w), 2031 (w), 1723 (w), 1622 (w), 1595 (w), 1556 (w), 1503 (s), 1405 (s), 1315 (m), 1250 (s), 1218 (s), 1098 (w), 981 (s), 930 (m), 867 (w), 812 (s), 779 (s) cm^{-1}; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 6.12$ (s, 6 H; C4-H(pz)), 1.38 ppm (bs, 108 H; *t*Bu-H); ^{1}H NMR (300 MHz, [D$_8$]toluene, −55 °C): $\delta = 6.20$ (s, C4-H(pz)), 6.05 (s), overlapping with 6.00 (bs, combined integration 6 H; C4-H(pz)), 1.37 (bs; *t*Bu-H), overlapping with 1.18 ppm (s, combined integration 108 H; *t*Bu-H); elemental analysis calcd (%) for $C_{66}H_{114}Ca_3N_{12}$ (1195.93): C 66.28, H 9.61, N 14.06; found C 64.85, H 9.56, N 13.58.

2: $[Sr_4(tBu_2pz)_8]$ (0.85 g, 95 %). M.p. (sealed tube/N_2): 348–353 °C; IR (Nujol): similar to **1**. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta =$ 6.00 (bs, 8 H; C4-H(pz)), 1.33 ppm (bd, 144 H; *t*Bu-H); ^{1}H NMR (300 MHz, [D$_8$]toluene, −60 °C): $\delta = 6.31$ (s, 2 H; C4-H(pz)), 6.16 (s, 2 H; C4-H(pz)), 6.08 (s, 4 H; C4-H(pz)), 1.48 ppm (s; *t*Bu-H), overlapped by 1.85–0.97 ppm (bm, 144 H combined intergration; *t*Bu-H); elemental analysis calcd (%) for $C_{88}H_{152}N_{16}Sr_4$ (1784.74): C 59.22, H 8.58, N 12.57; found C 58.19, H 8.49, N 12.41.

3: $[Ba_6(tBu_2pz)_{12}]$ (0.95 g, 96 %). M.p. (sealed tube/N_2): > 350 °C; IR (Nujol): similar to **1**. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta =$ 5.81 (s, 12 H; C4-H(pz)), 1.26 ppm (s, 272 H; *t*Bu-H); elemental analysis calcd (%) for $C_{132}H_{288}Ba_6N_{24}$ (2975.35): C 53.29, H 7.72, N 11.30; found C 52.70, H 7.67, N 11.15.

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[1] a) J. E. Cosgriff, G. B. Deacon, *Angew. Chem.* **1998**, *110*, 298–299; *Angew. Chem. Int. Ed.* **1998**, *37*, 286–287; b) F. Nief, *Eur. J. Inorg. Chem.* **2001**, 891–904.

[2] a) D. Pfeiffer, B. J. Ximba, L. M. Liable-Sands, A. L. Rheingold, M. J. Heeg, D. M. Coleman, H. B. Schlegel, T. F. Kuech, C. H. Winter, *Inorg. Chem.* **1999**, *38*, 4539–4548; b) G. B. Deacon, C. M. Forsyth, A. Gitlits, R. Harika, P. C. Junk, B. W. Skelton, A. H. White, *Angew. Chem.* **2002**, *114*, 3383–3385; *Angew. Chem. Int. Ed.* **2002**, *41*, 3249–3251; c) G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Bürgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127–138.

[3] a) C. Yelamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 3892–3894; b) G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 2372–2373; *Angew. Chem. Int. Ed.* **1998**, *37*, 2251–2252; c) G. B. Deacon, E. E. Delbridge, D. J. Evans, R. Harika, P. C. Junk, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2004**, *5*, 1193–1204, and references herein; d) G. B. Deacon, E. E. Delbridge, C. M. Forsyth, *Angew. Chem.* **1999**, *111*, 1880–1882; *Angew. Chem. Int. Ed.* **1999**, *38*, 1766–1767; e) R. Falvello, J. Fornies, A. Martin, R. Navarro, V. Sicilia, P. Villarroya, *Chem. Commun.* **1998**, 2429–2430; f) J. R. Perera, M. J. Heeg, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1999**, *121*, 4536–4537; g) D. Pfeiffer, M. J. Heeg, C. H. Winter, *Angew. Chem.* **1998**, *110*, 2674–2676; *Angew. Chem. Int. Ed.* **1998**, *37*, 2517–2519.

[4] a) J. Hitzbleck, G. B. Deacon, A. Y. O'Brien, K. Ruhlandt-Senge, *Chem. Eur. J.* **2004**, *10*, 3315–3323; b) J. Hitzbleck, G. B. Deacon, A. Y. O'Brien, K. Ruhlandt-Senge, provisional patent application, **2003**.

[5] D. Pfeiffer, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **2000**, *39*, 2377–2384.

[6] A. Y. O'Brien, J. Hitzbleck, K. Ruhlandt-Senge, unpublished results.

[7] **1**: $C_{66}H_{114}Ca_3N_{12}$; $Mr = 1195.94$. Triclinic *P-1*, $a = 13.8474(2)$, $b = 14.0132(2)$, $c = 20.2472(4)$ Å, $\alpha = 75.185(1)°$, $\beta = 77.698(1)°$, $\gamma = 75.725(1)°$, $V = 3633.5(1)$ Å^3, $\rho_{(calcd)}$ $(Z = 2) = 1.093$ g cm^{-3}; $N_t = 49616$, $N = 12763$ unique ($R_{int} = 0.0672$), $N_o = 8489$ ($2\theta_{max} = 50°$); $R = 0.0728$, $Rw = 0.1705$.**2:** $C_{88}H_{152}N_{16}Sr_4$; $Mr = 1784.74$. Triclinic *P*-1, $a = 13.149(1)$, $b = 13.508(1)$, $c = 15.701(1)$ Å, $\alpha = 77.652(2)°$, $\beta = 73.123(2)°$, $\gamma = 66.040(2)°$, $V = 2424.0(4)$ Å^3; $\rho_{(calcd)}$ $(Z = 1) = 1.217$ g cm^{-3}; $N_t = 19969$, $N = 8542$ (Rint = 0.0358), $N_o = 5885$ ($2\theta_{max} = 50°$); $R = 0.0707$, $Rw = 0.1831$. **3:** $C_{132}H_{288}Ba_6N_{24}$, $Mr = 2975.35$. Triclinic *P*-1, $a = 13.1215(2)$, $b = 13.5635(2)$, $c = 23.4625(4)$ Å, $\alpha = 74.172(1)°$, $\beta = 81.333(1)°$, $\gamma = 66.707(1)°$, $V = 3685.61(11)$ Å^3; $\rho_{(calcd)}$ $(Z = 1) = 1.309$ g cm^{-3}; $N_t = 54705$, $N = 12948$ (Rint = 0.0468), $N_o = 9220$ ($2\theta_{max} = 50°$); $R = 0.0922$, $Rw = 0.1749$. CCDC 222108–222110 (**1**–**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.hmtl (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax; (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[8] A. F. Wells, *Structural Inorganic Chemistry, 5th Ed.*, Clarendon, Oxford, **1984.**

[9] L. Pauling, *The Nature of the Chemical Bond, 3rd Ed.*, Cornell University Press, Ithaca, **1960**.

[10] a) R. Zerger, G. Stucky, *J. Organomet. Chem.* **1974**, *80*, 7–17; b) R. A. Williams, T. P. Hanusa, J. C. Huffman, *Organometallics* **1990**, *9*, 1128–1134.

[11] G. B. Deacon, C. M. Forsyth, A. Gitlits, B. W. Skelton, A. H. White, *Dalton Trans.* **2004**, *8*, 1239–1247.

[12] A. Steiner, G. T. Lawson, B. Walfort, D. Leusser, D. Stalke, *Dalton Trans.* **2001**, *3*, 219–221.

[13] J. Hitzbleck, K. Ruhlandt-Senge, G. B. Deacon, in preparation.

[14] a) R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, 751–767; b) S. Harder, *Angew. Chem.* **2004**, *116*, 2768–2773; *Angew. Chem. Int. Ed.* **2004**, *43*, 2714–2718.

[15] G. B. Deacon, A. Gitlits, B. W. Skelton, A. H. White, *Chem. Commun.* **1999**, 1213–1214.

[16] J. Elguero, E. Gonzalez, R. Jacquier, *Bull. Soc. Chim. Fr.* **1968**, 707–713.