73938(4) Å^3, $Z=48$, $\rho=1.365$ g cm^{-3}, $2\theta_{max}=41.22°$, $\mu=1.542$ mm^{-1}, $T=223(2)$ K; Siemens Smart CCD diffractometer; Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å); of 25657 reflections measured, 692 were independent, R(int.) = 0.0323. The structure was solved by direct methods and refined by a full-matrix least-squares procedure against F^2 (hydrogen atoms were not refined) with SHELXTL (Version 5.03, G. M. Sheldrick); $R=0.0558$, $wR^2=0.1547$ for 679 reflections with $I>4\sigma(I)$, 68 parameters, GOF = 1.164; max./min. residual electron density 0.687/ – 0.501 e Å^3. Semiempirical absorption correction applied. All other F-centered space groups (centro and non-centrosymmetric) were investigated, but none remove any of the disorder. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112388. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[22] A. K. Brimah, E. Siebel, R. D. Fischer, N. A. Davies, D. C. Apperley, R. K. Harris, *J. Organomet. Chem.* **1994**, *475*, 85 – 94.

[23] A. Bonardi, C. Carini, C. Pelizzi, G. Pelizzi, G. Predieri, P. Tarasconi, M. A. Zoroddu, K. C. Molloy, *J. Organomet. Chem.* **1991**, *401*, 283 – 294.

[24] E. Siebel, R. D. Fischer, J. Kopf, N. A. Davis, D. C. Apperley, R. K. Harris, *Inorg. Chem. Commun.* **1998**, *1*, 346 – 349.

[25] R. Uson, J. Fornies, M. A. Uson, E. Lalinde, *J. Organomet. Chem.* **1980**, *185*, 359 – 366.

[26] C. Glidewell, D. C. Liles, *Acta Crystallogr. Sect. B* **1978**, *34*, 129 – 134.

Templated Synthesis of Vanadium Borophosphate Cluster Anions**

Ranko P. Bontchev, Junghwan Do, and Allan J. Jacobson*

Early transition metals are well known to form complex polyoxoanions with ring and cage structures,[1] including some exceptionally large ring-shaped molybdenum oxide clusters that have recently been reported.[2] Other cluster compounds contain arsenate, organophosphonate, and borate anions in addition to metal oxo species.[3] Several of these cluster anions encapsulate anions,[4] molecules,[5] or cations,[6] and in some cases the size and shape of the cage has been shown to depend on the size of a specific ion present in the synthesis. For example, the Preyssler anion, $[NaP_5W_3O_{110}]^{14-}$, is not formed in the absence of Na^+.[7] Similarly, ClO_4^- and N_3^- anions apparently act as templates in the formation of $[HV_{22}O_{54}(ClO_4)]^{6-}$ and $[H_2V_{18}O_{44}(N_3)]^{5-}$.[8]

In the last few years a number of metal borophosphates have been synthesized and structurally characterized.[9] Three new vanadium borophosphates have been described recently: the three-dimensional framework **I**[10] and two compounds containing cluster anions, **II**[11] and **III**.[12] Here we report the

$(H_3NCH_2CH_2NH_3)_2[(VO)_5(H_2O)BO_2(PO_4)_2]\cdot 1.5\,H_2O$ **I**

$(N_2C_6H_{14})_2[VO(PO_3OH)_4(B_3O_3OH)]\cdot 4\,H_2O$ **II**

$(H_3NCH_2CH_2NH_3)_2[Na\supset\{(VO)_2BO_2(PO_3OH)_2\}_5]\cdot 22.5\,H_2O$ **III**

$(C_4H_{12}N_2)_6[(VO)_2BP_2O_{10}]_4\cdot n\,H_2O$ **1** ($n=2, 6, 14$)

$Na_{14}[Na\supset\{(VO)_2BP_2O_{10}\}_5]\cdot n\,H_2O$ **2**

$A_{17}[A\supset\{(VO)_2BP_2O_{10}\}_6]\cdot n\,H_2O$ **3** ($A = NH_4^+, K^+, Rb^+, Cs^+$)

synthesis and structures of the new vanadium borophosphates **1**, **2**, and **3** containing cluster anions with different ring sizes, and show that the ring size of the anion is determined by the size of the cation used in the synthesis. Compound **III**, which was recently obtained in a low-yield synthesis,[12] contains a cluster anion similar to that found in **2**.

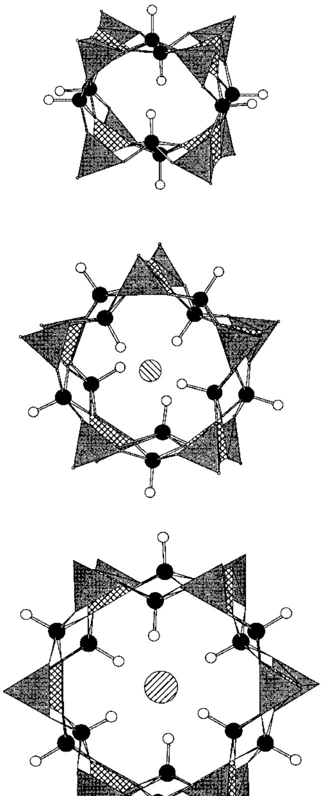


Figure 1. The cyclic cluster anions present in **1** (top), **2** (middle), and **3** (bottom). The PO_4 and BO_4 units are shown as filled and crosshatched tetrahedra, vanadium and oxygen atoms as filled and open circles, and sodium and nitrogen atoms as hatched circles.

Hydrothermal reactions of V_2O_3, H_3BO_3, and the appropriate phosphate salt at 180 °C for three days gave crystals of **1**, **2**, and **3**. The compounds were characterized by single-crystal X-ray diffraction. The structure of **1** ($n=6$) contains the cluster anion $[(VO)_2BP_2O_{10}]_4^{12-}$ (Figure 1, top).[13] Each tetravalent vanadium atom in the cluster anion is coordinated by five oxygen atoms in a square-pyramidal arrangement with one short V=O distance characteristic of a vanadyl group. Two VO_5 pyramids share a common edge to form V_2O_8 dimers of two distinct types in equal number. In one dimer (V3, V4; Figure 2) the two V=O groups are in a *cis* orientation and point outwards from the center of the cluster. In the other dimer (V1, V2) the V=O groups are in a *trans* orientation. Two oxygen atoms related by a center

---

[*] Prof. A. J. Jacobson, Dr. R. P. Bontchev, J. Do
Department of Chemistry
University of Houston
Houston, TX 77204-5641 (USA)
Fax: (+1) 713-743-2787
E-mail: ajjacob@uh.edu

[**] This work was supported in part by the National Science Foundation under Grant DMR-9214804 and by the Robert A. Welch Foundation. The work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation under Award Number DMR-9632667 and the Texas Center for Superconductivity at the University of Houston.

1433-7851/99/3813-1937 $ 17.50+.50/0

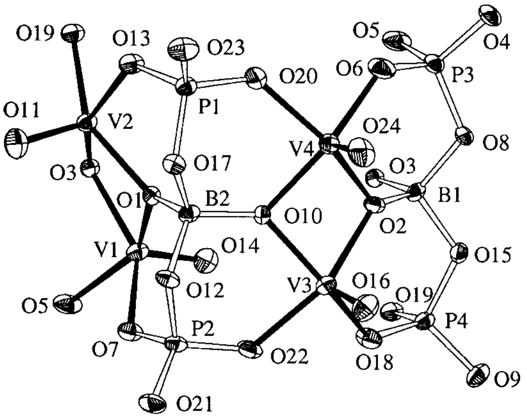


Figure 2. The coordination environments of the vanadium, phosphorus, and boron atoms in **1**. The thermal ellipsoids are shown at the 50% probability level.

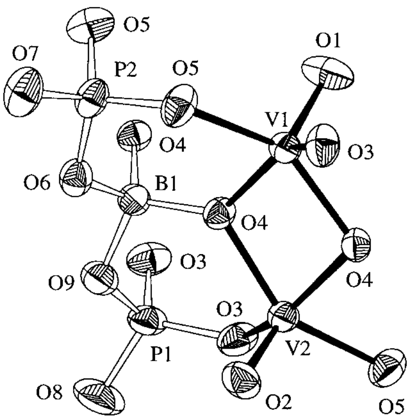


Figure 3. The coordination environments of the vanadium, phosphorus, and boron atom in **3**. The thermal ellipsoids are shown at the 50% probability level.

of symmetry, one from each of the two *trans* dimers, point into the center of the anion. The *trans* orientation minimizes nonbonded oxygen–oxygen repulsions and is usually observed for V_2O_8 dimers. For example, in the recently reported compound **I** the V=O groups also adopt a *trans* orientation in closely similar structural units.[10] In the present case, insufficient space is available inside the cluster anion to accommodate more than two oxygen atoms, and consequently the V=O groups in two of the dimers are forced into a *cis* orientation. The basal planes of the VO_5 square pyramids in the *cis*-oriented V_2O_8 dimers are tilted at an angle of 169.5° to give a reasonable nonbonded O–O contact of 3.175 Å. Bond valence calculations give values of 4.04, 4.08, 4.10, and 4.15 for the four nonequivalent vanadium atoms.

Two PO_4 tetrahedra and a BO_4 tetrahedron are connected through common corners to form BP_2O_{10} trimers (Figure 2). In each trimer, two phosphorus-bound oxygen atoms are unshared. The BP_2O_{10} trimers and V_2O_8 dimers are connected by sharing oxygen atoms to give a building unit of composition $(VO)_2BP_2O_{10}$. Two phosphorus oxygen atoms are also bound to vanadium atoms in P-O-V connections, and one boron-bound oxygen atom adopts a μ^3-O arrangement with bonds to two vanadium atoms. In **1**, four of these $(VO)_2BP_2O_{10}$ units are connected in a cyclic fashion to form a four-ring of composition $[(VO)_2BP_2O_{10}]_4{}^{12-}$. In the three-dimensional structure, the four-rings of the cluster anion are oriented perpendicular to each other. The cluster ion charge is balanced by diprotonated piperazine molecules and water molecules occupy the remaining lattice volume.

If piperazine is replaced by $NH_4{}^+$ in a similar hydrothermal synthesis reaction, a cluster anion is obtained containing the same $(VO)_2BP_2O_{10}$ building unit found in **1**, but with a larger ring size (Figure 1, bottom). The structure of **3** ($A = NH_4{}^+$) also contains a cyclic anion which is formed by condensation of six $(VO)_2BP_2O_{10}$ building units and is centered by an ammonium ion. Similar compounds **3** ($n \approx 12$) containing six-rings centered by the corresponding cation A are obtained from reactions with $A = K^+$, Rb^+, and Cs^+.

In **3** (Figure 3), the vanadium atoms (V1, V2) and vanadyl oxygen atoms (O3, O2) are disordered equally over two positions, giving two possible orientations for the VO_5 square pyramids in each dimer. As noted above, the *trans* orientation is considered more likely (Figure 1, bottom; the orientations of adjacent V=O units are also assumed to alternate around the anion ring). The other possible arrangement results in unfavorable O–O nonbonded contacts (2.371 Å). In contrast to **1**, the cluster anions in **3** are oriented with the rings parallel to each other in the three-dimensional structure. Bond valence calculations give values of 4.08 and 4.12 for V1 and V2, respectively.

The presence of a cation centering the cluster anion in **3** is an important difference between the anions in **1** and **3**. The anion in **3**, formed from six $(VO)_2BP_2O_{10}$ building units, has enough space in the center to include a cation and enough flexibility to accommodate cations over a limited size range (K^+ (1.38 Å) to Cs^+ (1.67 Å)). The cluster anion in **1** is formed in the absence of any small cation and is not centered. The $(\text{piperazineH}_2)^{2+}$ countercations in **1** apparently cannot stabilize a still larger cluster anion. A comparison of the anions in **1** and **3** suggests that the included cation acts as a template in the formation of the six-ring. To confirm this, we have investigated the use of Na^+ (1.02 Å) as the templating cation in the synthesis of the five-ring structure previously reported.[12] To confirm this, we have investigated the use of Na^+ (1.02 Å) as the templating cation.

Using reaction conditions identical to those for the synthesis of **3**, but substituting Na_2CO_3 for NH_4OH, we obtained in high yield a pure phase of **2**, as was shown by single-crystal X-ray diffraction. In **2** the five building $(VO)_2BP_2O_{10}$ units are arranged in a cyclic cluster anion centered by a Na^+ cation (Figure 1, middle). Due to the odd number of V_2O_8 dimers, two pairs of neighboring vanadyl oxygen atoms necessarily appear in a *cis* configuration. The anion is closely similar to the anion previously reported in $(C_2N_2H_{10})_2[(Na(VO)_{10}(BP_2O_{10}H_2)]$[12] and is not described in detail here.

The thermogravimetric studies showed that all samples lose their water molecules between room temperature and 200 °C. The structures collapse on loss of water and the samples become amorphous, as indicated by powder X-ray diffraction. Between 200 and 400 °C all the organic and/or NH_3 molecules are lost, and a glassy matrix composed of VO_2, P_2O_5, B_2O_3, and M_2O (M = Na, K, Rb, Cs) is formed.

1433-7851/99/3813-1938 $ 17.50+.50/0

The variations in the magnetic susceptibility and effective magnetic moment for **3** are shown in Figure 4. At higher temperatures ($120 < T < 280$ K) the sample is paramagnetic and obeys the Curie law with $\mu_{eff} = 1.74\,\mu_B$, which is close to the value of $1.73\,\mu_B$ expected for V^{4+} ($3d^1$, $S = 1/2$). Below 120 K, the magnetic properties are dominated by antiferromagnetic interactions within isolated V^{4+}–V^{4+} dimers, and the susceptibility goes through a maximum at about 60 K. The width of the maximum, however, is broader than expected from a dimer with a single exchange constant. The small upturn in the magnetic susceptibility at low temperature is most likely due to the presence of a small number of isolated V^{IV} defects. The magnetic susceptibility data for **1** also indicate antiferromagnetic interactions, but the maximum in the susceptibility occurs at even higher temperature. The present data suggest additional interactions between adjacent dimers. A more detailed analysis of the susceptibility data for the three clusters and correlation of the results with the structural features will be reported elsewhere.

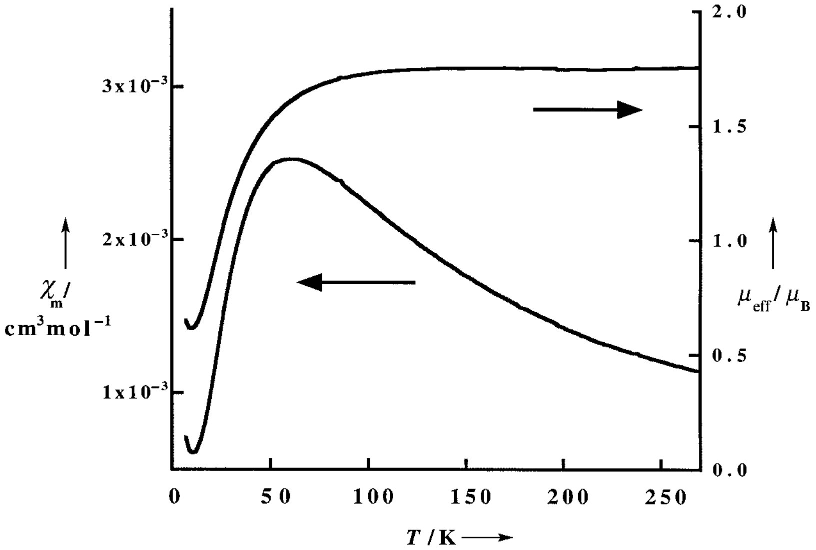


Figure 4. The molar magnetic susceptibility χ_m and the effective magnetic moment μ_{eff} of **3** as a function of temperature.

In conclusion, we have demonstrated a template-directed synthesis of vanadium borophosphate cluster anions of different sizes. Synthesis of larger vanadium borophosphate cluster anions by careful selection of templates of appropriate size is currently being investigated.

Experimental Section

General: The hydrothermal synthesis were carried out in Teflon-lined steel autoclaves at 160°C for three days. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN. The IR spectra were measured in the range 400–4000 cm^{-1} with KBr pellets on a Galaxy FTIR 5000 spectrometer. Thermogravimetric analyses were carried out at a heating rate of 2 Kmin^{-1} in air with a TA Instruments TGA 2950 Thermogravimetric Analyzer. Magnetic data were measured in the range $4 < T < 290$ K, $H = 0.1$ T, on a Quantum Design MPMS SQUID XL Magnetometer.

1: V_2O_3 (0.125 g, 0.8 mmol), H_3BO_3 (0.103 g, 1.7 mmol), H_3PO_4 (0.11 mL, 1.6 mmol, 80 wt% solution in H_2O), piperazine (0.1436 g, 1.7 mmol), and H_2O (2 mL) were allowed to react. The solution pH values before and after the reaction were 7.42 and 8.07, respectively. Reaction products: rod-shaped deep blue crystals of **1** ($n = 2$), average size 0.1–0.3 mm, yield approximately 30% based on vanadium, together with blue crystals of **1** ($n = 6$) in about 40% yield (elemental analyses calcd: N 7.99, V 19.37, P 11.78, B 2.06; found: N 8.24, V 20.51, P 11.05, B 1.94) and pale blue plates of **1** ($n = 14$) in about 5% yield. **1**: IR: $\tilde{\nu} = 466$ (w), 604 (m), 690 (w), 717 (m), 888 (sh), 940 (s), 978 (sh), 1047 (s), 1156 cm^{-1} (m).

2: V_2O_3 (0.2248 g, 1.5 mmol), H_3BO_3 (0.3090 g, 5 mmol), H_3PO_4 (0.342 mL, 5 mmol, 85 wt% solution in H_2O), Na_2CO_3 (0.5299 g, 10 mmol), and H_2O (2 mL) were allowed to react. The solution pH values before and after the reaction were 8.25 and 8.90, respectively. The product was filtered, and the dark blue filtrate was left to crystallize at room temperature for one week. Transparent blue crystals of **2** were obtained as a single phase. **2**: IR: $\tilde{\nu} = 543$ (m), 608 (m), 731 (w), 896 (sh), 955 (s), 991 (s), 1043 (s), 1164 cm^{-1} (sh).

3 ($A = NH_4^+$): V_2O_3 (0.2248 g, 1.5 mmol), H_3BO_3 (0.3090 g, 5 mmol), H_3PO_4 (0.342 mL, 5 mmol, 85 wt% solution in H_2O), NH_4OH (2 mL, 15.4 mmol, 29.6% solution in H_2O), and H_2O (2 mL) were allowed to react. The solution pH values before and after the reaction were 7.53 and 8.80, respectively. Reaction product: transparent blue crystals of **3** ($A = NH_4^+$), average size 0.1–0.3 mm, yield 66.3% based on vanadium (elemental analyses calcd ($n = 12$): N 9.20, V 22.30, P 13.56, B 2.37; found: N 9.03, V 20.36, P 12.20, B 2.20). The K, Rb, and Cs analogues were synthesized using the same reaction conditions and reactant molar ratios with the corresponding alkali metal carbonates. All compounds were obtained as single-phase products. **3**: IR: $\tilde{\nu} = 463$ (m), 546 (w), 615 (m), 683 (w), 729 (w), 901 (w), 960 (s), 995 (s), 1032 (s), 1169cm^{-1} (s).

Received: March 3, 1999 [Z13106IE]
German version: *Angew. Chem.* **1999**, *111*, 2063–2066

Keywords: boron · cluster compounds · hydrothermal synthesis · phosphorus · template synthesis · vanadium

---

[1] a) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; b) W. G. Klemperer, T. A. Marquart, O. M. Yaghi, *Angew. Chem.* **1992**, *104*, 51; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 49.

[2] c) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, C. Beugholt, P. Kögerler, C. Lu, *Angew. Chem.* **1998**, *110*, 1278; *Angew. Chem. Int. Ed.* **1998**, *37*, 1220; b) A. Müller, M. Koop, H. Bögge, M. Schmidtmann, C. Beugholt, *Chem. Commun.* **1998**, 1501; c) C.-C. Jiang, Y.-G. Wei, Q. Liu, S-W. Zhang, M.-C. Shao, Y.-Q. Tang, *Chem. Commun.* **1998**, 1937.

[3] a) A. Müller, J. Döring, *Angew. Chem.* **1988**, *100*, 1789; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1721; b) A. Müller, J. Döring, H. Bögge, *J. Chem. Soc. Chem. Commun.* **1991**, 273; c) G. Huan, M. A. Greaney, A. J. Jacobson, *J. Chem. Soc. Chem. Commun.* **1991**, 260; d) A. Müller, E. Krickemeyer, S. Dillinger, H. Bögge, A. Stammler, *J. Chem. Soc. Chem. Commun.* **1994**, 2539; e) G. Huan, A. J. Jacobson, V. W. Day, *Angew. Chem.* **1991**, *103*, 426; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 421; f) Q. Chen, J. Zubieta, *J. Chem. Soc. Chem. Commun.* **1994**, 1635; g) Q. Chen, J. Zubieta, *J. Chem. Soc. Chem. Commun.* **1994**, 2663; h) J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter, J. Zubieta, *Angew. Chem.* **1997**, *109*, 1049; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1008; i) T. Yamase, M. Suzuki, K. Ohtaka, *J. Chem. Soc. Dalton Trans.* **1997**, 2463.

[4] a) A. Müller, E. Krickemeyer, M. Penk, H.-J. Walberg, H. Bögge, *Angew. Chem.* **1989**, *99*, 1060; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1045; b) D. D. Heinrich, K. Folting, W. E. Strieb, J. C. Huffman, G. Christou, *J. Chem. Soc. Chem. Commun.* **1989**, 1411; c) A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer, J. Döring, *Angew. Chem.* **1990**, *102*, 927; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 926; d) A. Müller, R. Rohlfing, J. Döring, M. Penk, *Angew. Chem.* **1991**, *103*, 575; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 588.

[5] a) R. Contant, A. Tézé, *Inorg. Chem.* **1985**, *24*, 4610; b) A. Müller, K. Hovemeier, R. Rohlfing, *Angew. Chem.* **1992**, *104*, 1214; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1192.

[6] a) V. W. Day, W. G. Klemperer, O. M. Yaghi, *J. Am. Chem. Soc.* **1989**, *111*, 5959; b) A. Müller, J. Döring, *Z. Anorg. Allg. Chem.* **1991**, *595*, 251.

[7] M. H. Alizadeh, S. P. Harmalker, Y. Jeannin, J. Martin-Frère, M. T. Pope, *J. Am. Chem. Soc.* **1985**, *107*, 2662.

[8] a) A. Müller, E. Krickemeyer, M. Penk, R. Rohlfing, A. Armatage, H. Bögge, *Angew. Chem.* **1991**, *103*, 1720; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1674; b) A. Müller, E. Diemann, E. Krickemeyer, *Naturwissenschaften* **1993**, *80*, 77.

[9] R. Kniep, H. Engelhardt, C. Hauf, *Chem. Mater.* **1998**, *10*, 2930, and references therein.

[10] C. J. Warren, R. C. Haushalter, D. J. Rose, J. Zubieta, *Chem. Mater.* **1997**, *9*, 2694.

[11] R. Bontchev, J. Do, A. J. Jacobson, *Inorg. Chem.* **1999**, *38*, 2231.

[12] C. J. Warren, R. C. Haushalter, D. J. Rose, J. Zubieta, *Inorg. Chem. Commun.* **1998**, *1*, 4.

[13] Crystal structure analyses: a) **1** ($n=6$) at $T=293$ K: monoclinic, space group $P2_1/n$ (no. 14), $a=12.9822(9)$, $b=16.2608(12)$, $c=17.0246(11)$ Å, $\beta=103.412(2)^\circ$, $V=3495(9)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.998$ g cm^{-1}; diffractometer: Siemens SMART 1 K CCD (Mo$_{K\alpha}$ radiation, graphite monochromator); $\mu=1.329$ mm^{-1}; a hemisphere of data (1271 frames at 5-cm detector distance), narrow-frame method with scan widths of 0.30° in ω and exposure time of 30 s per frame, $2\theta_{\max}=53.96^\circ$, 9372 measured reflections, 5582 independent reflections; corrections for Lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate. The program SADABS[14a] was used for the absorption correction; structure solved by direct methods (SHELXTL[14b]) and refined by least-squares methods (all atoms anisotropic, SHELXTL[14c]); 502 free parameters; GOF = 1.126, R values ($I>2\sigma(I)$): $R1=0.057$, $wR2=0.106$; max./min. residual electron density: $0.586/-0.436$ e^{-1} Å^{-3}.[15] b) **1** ($n=2$): deep blue crystal, space group $P2_1/c$, $a=10.9147(7)$, $b=11.9186(7)$, $c=25.3828(15)$ Å, $\beta=95.011(1)^\circ$, $V=3289(9)$ Å^3. c) **1** ($n=14$): pale blue crystal, space group $P2_1/c$, $a=13.2229(7)$, $b=28.7520(16)$, $c=21.2716(11)$ Å, $\beta=98.916(1)^\circ$, $V=7989(13)$ Å^3. d) **3** ($\text{A}=\text{NH}_4^+$, $n=12$) at $T=293$ K: rhombohedral, space group $R\bar{3}m$ (no. 166), $a=14.116(2)$ Å, $\alpha=71.96(2)^\circ$, $V=2470.7(5)$ Å^3, $Z=1$, $\rho_{\text{calcd}}=1.651$ g cm^{-1}; data collection, corrections and structure solution as above for **1** ($n=6$); $\mu=1.376$ mm^{-1}, 2689 measured reflections, 1487 independent reflections; 147 free parameters; GOF = 1.037, R values ($I>2\sigma(I)$): $R1=0.056$, $wR2=0.151$; max./min. residual electron density: $0.415/-0.370$ e^{-1} Å^{-3}.[15] e) **2** at $T=293$ K: monoclinic, space group $P2_1/n$ (no. 14), $a=22.198(1)$, $b=15.3947(8)$, $c=26.118(1)$ Å, $\beta=115.113(1)^\circ$, $V=8081.8(8)$ Å^3. f) Crystallographic data (excluding structure factors) for the structures of **1** and **3** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115529 and -115530. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

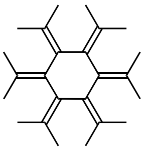
[14] a) G. M. Sheldrick, Program SADABS, Universität Göttingen, **1995**; b) G. M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-ray Instruments, Madison, WI, **1995**; c) G. M. Sheldrick, SHELX-96 Program for Crystal Structure Determination, **1996**.

[15] Selected bond lengths [Å] and angles [°] for **1** ($n=6$): V–O 1.932–2.001, V=O 1.588–1.613, P–O 1.497–1.579, B–O 1.452–1.497; O-P-O 105.5–114.0, O-B-O 104.5–112.4; for **3** ($\text{A}=\text{NH}_4^+$, $n=12$): V–O 1.932–2.022, V=O 1.590, P–O 1.496–1.569, B–O 1.461–1.480; O-P-O 107.5–112.0, O-B-O 105.1–111.0.

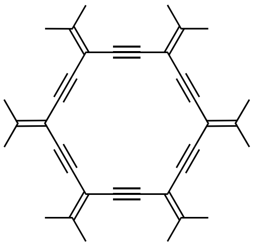
Expanded Radialenes: Modular Synthesis and Characterization of Cross-Conjugated Enyne Macrocycles[**]

Sara Eisler and Rik R. Tykwinski[*]

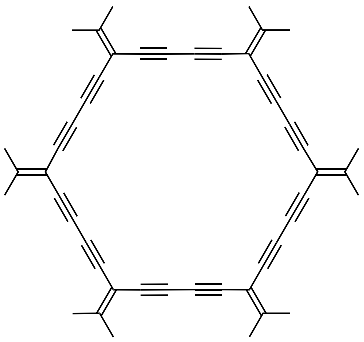
Structurally intermediate between the radialenes **1**[1] and expanded radialenes **3**[2] are a class of hitherto unknown enyne macrocycles **2** constructed of 3-alkylidene-1-propynyl [−C≡C−C(=CR$_2$)−] building blocks.[3] Our interest in the electronic effects of cross-conjugation[4] in iso-polydiacetylenes (iso-PDAs, **4**), the acyclic analogues of **2**, led us to explore the synthesis of macrocycles such as **2** with a view to extending our understanding of π-electron delocalization in this intriguing class of molecules.



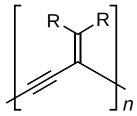
1



2



3



4

Our initial studies of the electronic absorption behavior of iso-PDAs showed that π-electron delocalization in these compounds is not limited to the longest linearly conjugated segment; instead, it increases as a function of oligomer length and reaches saturation around the length of the nonamer (**4**; R = Me, $n=9$).[5] This analysis suggested a subtle contribution from cross-conjugation to the overall electronic communication along the enyne framework of iso-PDAs. It was anticipated that the more structurally rigid enyne framework of **2** would allow evaluation of electronic effects from cross- or

---

[*] Prof. R. R. Tykwinski, S. Eisler
Department of Chemistry
University of Alberta
Edmonton, AB T6G 2G2 (Canada)
Fax: (+1) 780-492-8231
E-mail: rik.tykwinski@ualberta.ca

[**] This work was supported by a Gen-Science Endowment from the University of Alberta and by NSERC of Canada. We thank Y. Zhao for the initial synthesis of **13**.

1433-7851/99/3813-1940 $ 17.50+.50/0