It is interesting to contrast this with the case for $Fe(Cp)(CO)_2I$, where spectroscopic evidence points to silver adduct formation via an iodide donor.[13] This can be understood in terms of coordinative saturation of the iron atom. A hybrid case occurs with $[PtCl_2(C_6F_5)_2]^{2-}$, where an $[Ag(PPh_3)]^+$ adduct takes an intermediate structure; the silver atom is bonded primarily to Cl but also to Pt.[6]

The present findings raise some interesting questions about the mechanism(s) of silver salt metathesis reactions and suggest the possibility of metal–metal-bonded intermediates. The unconsummated metathesis seen with $Ag[B_{11}CH_{12}]$ and $IrCl(CO)(PPh_3)_2$ suggests that the carborane anion has extremely low nucleophilicity.[14] Space-filling models do not support the possibility that the steric bulk of $B_{11}CH_{12}^-$ prevents the formation of $Ir(B_{11}CH_{12})(CO)(PPh_3)_2$. The anion has a smaller coordination bite than $PPh_3$. The low nucleophilicity of $B_{11}CH_{12}^-$ is the result of having no lone pairs and a very effective delocalization of charge. Only in donor solvents such as acetone does metathesis proceed, and then the product is the ionic $[Ir((CH_3)_2CO)(CO)(PPh_3)_2][B_{11}CH_{12}]$.[15] In this case the solvent is probably the entering nucleophile, which displaces $Cl^-$ so that precipitation of AgCl can drive the reaction. These results suggest that previously used weakly coordinating anions ($BF_4^-$, $ClO_4^-$, etc.) play a much more significant role in silver salt metathesis reactions than has been heretofore appreciated. For example, while $AgClO_4$ undergoes instant metathesis with $Ph_3SiCl$ in benzene, we find that $Ag[B_{11}CH_{12}]$ is inert. This suggests that the nucleophilicity of the anion is rate-determining. With $FeCp(CO)_2I$ and $Ag[B_{11}CH_{12}]$ in toluene we get rapid 1:1 adduct formation,[16] presumably with iodide as the donor to silver as suggested by Graham.[13a] The precipitation of AgI and ultimate formation of the metathesis product $Fe(Cp)(B_{11}CH_{12})(CO)_2$ takes several hours. Again, this suggests a rate-determining role for the anion even when heterolysis of the metal–halide bond is apparently assisted by bridging to silver. It is becoming clear that there can be considerably more mechanistic complexity to a metathesis reaction than is implied by its simple stoichiometry. The $B_{11}CH_{12}^-$ anion should be able to play a very useful role in detailed studies of metathesis mechanisms.

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**Supplementary Material Available:** Fractional crystal coordinates (Table IS), anisotropic thermal parameters (Table IIS), fixed hydrogen atom positions (Table IIIS), bond distances and angles for the coordination, respectively (Tables IVS and VS), and bond distances and angles for the phosphine and carborane anion, respectively (Tables VIS and VIIS) (13 pages); a listing of observed and calculated structure amplitudes (×10) (22 pages). Ordering information is given on any current masthead page.

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[13] (a) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (b) Salnikova, T. N.; Adrianov, V. G.; Struchkov, Y. T. *Koord. Khim.* **1976**, *2*, 707.

[14] Excess $Ag[B_{11}CH_{12}]$ gives some AgCl precipitate after several days, accompanied by decomposition.

[15] Anal. Calcd for $IrC_{41}H_{48}B_{11}P_2O_2$: C, 52.06; H, 5.12; P, 6.55. Found: C, 52.11; H, 5.30; P, 6.51. IR (KBr): 2550 (BH), 1978 (CO), 1632 (C=O) cm$^{-1}$.

[16] Anal. Calcd for $C_8H_{17}AgIrFeIO_2B_{11}$: C, 17.31; H, 3.09; I, 22.89. Found: C, 17.18; H, 2.79; I, 22.44. IR (KBr): 2042, 1990 (CO) cm$^{-1}$.

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## Soluble Metal Selenides. Synthesis and Structure of the Tridecaselenidodivanadate Anion, $V_2Se_{13}^{2-}$

*Sir:*

Soluble salts of transition-metal selenium anions $(M_xSe_y)^{z-}$ are rare, the known examples being $MSe_4^{2-}$ (M = Mo,[1] and W[2]) and $Fe_2Se_{12}^{2-}$[3] and the recently reported $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$ ions.[4] Even the related sulfur anions $(M_xS_y)^{z-}$ are limited in number, and among these most have M = Mo or W.[5] Of the sulfur and selenium anions in the vanadium triad only $VS_4^{3-}$[6] and $(M_6S_{17})^{4-}$ (M = Nb, Ta)[7] are known. We recently showed that some of the accessible anions in the W/Se system[4] differ markedly from those known in the W/S system. As a continuation of our efforts to discover new transition-metal selenium anions and to assess the relation of such ions to known solid-state materials, we report here the synthesis and structure of the $V_2Se_{13}^{2-}$ ion. This ion has both bridging and terminal $Se_2$ ligands as well as a bridging $Se_5$ ligand.

Dropwise addition of a toluene solution (20 mL) of bis(dimethyloctylsilyl) selenide[8] (3.5 g) into a mixture of $NH_4VO_3$ (0.5 g), $(NEt_4)Cl$ (2.1 g), and triethylamine (10 mL) in acetonitrile (20 mL) caused an immediate color change from white to brown. After stirring the solution at room temperature for 2 days, we obtained a precipitate from the brown solution. This brown material was readily recrystallized as black hexagonal-shaped plates suitable for X-ray characterization by slow diffusion of ether into acetonitrile.[9] Spectroscopic data suggested that this product is a vanadium–selenium compound.[10] The detailed nature of $(NEt_4)_2(V_2Se_{13})$ was established by single-crystal X-ray diffraction methods.[11]

The $V_2Se_{13}^{2-}$ ion (Figure 1) has pseudo-$C_s$ symmetry with heptacoordination at the V atoms. The V–V distance of 2.779 (5) Å is consistent with the presence of a V–V bond. The V atoms are bridged by two $Se_2$ ligands to form a $V_2(\mu\text{-}\eta^2\text{-}Se_2)_2$ core with average V–Se and Se–Se distances of 2.518 (6) and 2.305 (7) Å, respectively. The two V atoms are also linked by a $\mu$-$Se_5$ unit with an average V–Se distance of 2.505 (2) Å and two types of Se–Se bonds, two around the apical Se atom and two involving the Se atoms bonded to the V atoms, with average values of 2.350 (11) and 2.428 (3) Å, respectively. The coordination sphere of each V atom is completed by an unsymmetrically coordinated $\eta^2$-$Se_2$ ligand, with average V–Se distances of 2.403 (6) and 2.597 (9) Å and an average Se–Se distance of 2.334 (3) Å. The $V_2$-

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(1) Müller, A.; Krebs, B.; Diemann, E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 257–258.

(2) Lenher, V.; Fruekas, A. G. *J. Am. Chem. Soc.* **1927**, *49*, 3076–3080.

(3) Strasdeit, H.; Krebs, B.; Henkel, G. *Inorg. Chim. Acta* **1984**, *89*, L11–L13.

(4) Wardle, R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859–1860.

(5) Müller, A. *Polyhedron* **1986**, *5*, 323–339.

(6) Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731–6732 and references therein.

(7) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706–1713.

(8) Bis(dimethyloctylsilyl) selenide was prepared by mixing a 2:1 ratio of dimethyloctylsilyl chloride (Aldrich) and $Li_2Se$ in THF. Filtration of this suspension after stirring for 2 days at room temperature gave a yellowish solution. After solvent removal at 0.1 mmHg a clear yellow liquid remains, yield 90%.

(9) Recrystallization was performed by standard layering techniques in 8-mm glass tubes. In addition to the black hexagonal plates, white crystals of $(NEt_4)Cl$ were also obtained. Elemental analysis (Galbraith Laboratories, Inc.) of the crude product shows an expected low percentage of V and Se. The ratio found (Se:V = 6.1:1) is consistent with the formulation $V_2Se_{13}^{2-}$. From the percentage of vanadium in the crude sample a 20% yield of $(NEt_4)_2(V_2Se_{13})$ is estimated.

(10) IR (Nujol, CsI): $\nu$(V–Se), $\nu$(Se–Se) 392 (m), 340 (m), 320 (w), 298 (w) cm$^{-1}$. Attempts to obtain the $^{77}Se$ NMR spectrum of $V_2Se_{13}^{2-}$ failed owing to the quadrupole nature of adjacent $^{51}V$ nuclei; $I = {}^7/_2$, natural abundance 99.76%. No characteristic bands in the electronic spectrum were obtained from a DMF solution of the compound.

(11) Crystal data for $(NEt_4)_2(V_2Se_{13})$, $C_{16}H_{40}N_2Se_{13}V_2$: orthorhombic, $D_2^4$-$P2_12_12_1$, $Z = 4$, $a = 11.82$ (2) Å, $b = 13.20$ (2) Å, $c = 22.25$ (3) Å, $V = 3471$ Å$^3$ at −150 °C; 6679 reflections measured out to $2\theta$(Mo K$\alpha_1$) = 50°; $R = 0.053$ on 2237 reflections having $F_o^2 > 3\sigma(F_o^2)$.

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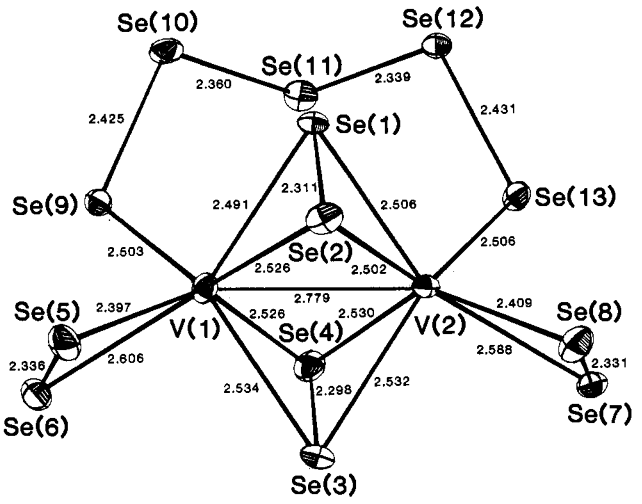

**Figure 1.** Structure of the $V_2Se_{13}^{2-}$ ion. 50% probability ellipsoids are shown and the estimated standard deviations in the V–V, V–Se, and Se–Se bond distances are 0.005, 0.004–0.005, and 0.003 Å, respectively.

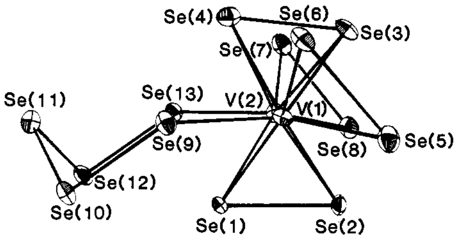

**Figure 2.** Another view of the $V_2Se_{13}^{2-}$ ion.

$(\mu$-$\eta^2$-$Se_2)_2$ core[12] found here also occurs in the solid-state compound $V_2Se_9$,[13] which consists of pseudo-one-dimensional infinite $(V_2Se_9)_x$ chains. The V atoms in $V_2Se_9$ associate in pairs with V–V distances alternating between 2.84 and 3.65 Å. The $V_2(\mu$-$\eta^2$-$Se_2)_2$ unit has a sulfur analogue $V_2(\mu$-$\eta^2$-$S_2)_2$, which is found in the mineral patronite $(VS_4)_n$.[14] In addition to the $\mu$-$\eta^2$-$Se_2$ unit, each V atom in the present molecular complex is further coordinated to an $\eta^2$-$Se_2$ ligand to form a $V_2(\mu$-$\eta^2$-$Se_2)_2(\eta^2$-$Se_2)_2$ core. It is possible to look upon the $V_2Se_9$ structure as an infinite chain of these $V_2(\mu$-$\eta^2$-$Se_2)_2(\eta^2$-$Se_2)_2$ units linked by a Se atom bridging the long V–V distance (3.65 Å). The presence of the $V_2(\mu$-$\eta^2$-$Se_2)_2(\eta^2$-$Se_2)_2$ unit in $V_2Se_{13}^{2-}$ and in $V_2Se_9$ demonstrates the persistence of this structural unit through molecular and solid-state systems.

In the $V_2Se_{13}^{2-}$ ion a $\mu$-$Se_5$ unit acts as a bidentate ligand bridging across two adjacent V atoms to form an interesting pseudo-seven-membered ring $V_2Se_5$. This ring adopts a chair conformation (Figure 2) similar to that of the $S_7$ ring.[15] In $Fe_2Se_2(Se_5)_2^{2-}$ [3] the $Se_5$ units are also bidentate, but each is coordinated to a single Fe atom to form a six-membered ring. However, the bridging bidentate $\mu$-$S_5$ unit is found in $Mo_2(NO)_2(S_2)_3(S_5)(OH)^{3-}$ [16] and $Nb_2(O)(OMe)_2(S_2)_3(S_5)^{2-}$.[17]

If one assigns charges as $Se_2^{2-}$ and $Se_5^{2-}$, then $V_2Se_{13}^{2-}$ contains $d^1$ $V^{4+}$ ions. Its structure is very similar to that of $(\eta^2$-$S_2)_2Mo(\mu$-$\eta^2$-$S_2)_2Mo(\eta^2$-$S_2)_2^{2-}$ (i.e., $Mo_2S_{12}^{2-}$ [18]), which can be thought of as containing two $d^1$ $Mo^{5+}$ ions and a Mo–Mo bond. The same overall charge is maintained in going from Mo to V by replacement of two terminal $Q_2^{2-}$ ligands with a single bridging $Q_5^{2-}$ ligand (Q = S or Se).

Although we have no information as yet on the mode of formation of the $V_2Se_{13}^{2-}$ ion, it is likely that reduction of $V^{5+}$ to $V^{4+}$ in the presence of $Se^{2-}$ leads to a variety of polyselenide species in solution, including the $Se_5^{2-}$ ion, which is selected out for steric reasons. The mode of formation and the reaction chemistry of the $V_2Se_{13}^{2-}$ ion are under further study.

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**Supplementary Material Available:** A listing of positional parameters (1 page). Ordering information is given on any current masthead page.

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(12) $V_2Se_{13}^{2-}$ is the only example of a molecular vanadium dinuclear species with two $\mu$-$\eta^2$-$Se_2$ groups across a V–V bond. The compound $V_2(Se_5)(C_5H_4CH_3)_2$ (V–V = 2.779 (4) and Se–Se = 2.295 (2) Å), which contains one such group across a V–V bond, has been described: Rheingold, A. L.; Bolinger, C. M.; Rauchfuss, T. B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1878–1880.

(13) Furuseth, S.; Klewe, B. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 467–471.

(14) Klemm, W.; Schnering, H. G. *Naturwissenschaften* **1965**, *52*, 12. Other examples are $V_2(\mu$-$S_2)_2(i$-$Bu_2NCS_2)_4$ (Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6347–6438) and $V_2(S_5)(C_5H_4CH_3)_2$ (Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551–1553).

(15) Kawada, V. I.; Hellner, E. *Angew. Chem.* **1970**, *82*, 390.

(16) Müller, A.; Eltzner, W.; Bögge, H.; Krickemeyer, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 884–885.

(17) Müller, A.; Schimanski, J.; Römer, M.; Bögge, H.; Baumann, F.-W.; Eltzner, W.; Krickemeyer, E.; Billerbeck, U. *Chimia* **1985**, *39*, 25–27.

(18) Müller, A.; Nolte, W.-O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835–2836.