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ELECTRON-TRANSFER REACTIONS OF DIVALENT YTTERBIUM METALLOCENES: SYNTHESIS OF THE SERIES [(Me₅C₅)₂Yb]₂[E] WHERE E IS O, S, Se, OR Te AND THE CRYSTAL STRUCTURE OF [(Me₅C₅)₂Yb]₂ [Se.]

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THE CRYSTAL STRUCTURE OF [(Me₅C₅)₂Yb]₂[μ-Se]**

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A. Zalkin

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LBL-22934

Electron-Transfer Reactions of Divalent Ytterbium Metallocenes;
Synthesis of the Series $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-E}]$ where E is O, S, Se,
or Te and Crystal Structure of $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Se}]$

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Abstract

The preparation of the divalent, base-free compounds, $(\text{Me}_5\text{C}_5)_2\text{M}$ where $\text{M} = \text{Eu}$ or Sm , from their respective diethyl ether complexes is described. Reaction of $(\text{Me}_5\text{C}_5)_2\text{M}$, where $\text{M} = \text{Yb}$ or Sm with N_2O gives $[(\text{Me}_5\text{C}_5)_2\text{M}]_2[\mu\text{-O}]$ in high yield. Additionally, $(\text{Me}_5\text{C}_5)_2\text{Yb}$ reacts with Ph_3PS or As_2S_3 or COS , Ph_3PSe or elemental Se , $n\text{-Bu}_3\text{PTe}$ or elemental Te , to give the bridging chalcogenides $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-E}]$ where E is S , Se , or Te , respectively. Magnetic susceptibility studies show that there is no magnetic exchange between the paramagnetic f-metals across the bridging group 16 dianions. The variable temperature magnetic studies also show that $(\text{Me}_5\text{C}_5)_2\text{Sm}$ and $[(\text{Me}_5\text{C}_5)_2\text{Sm}]_2[\mu\text{-O}]$ display temperature independent paramagnetism as predicted by Van Vleck. The crystal structure of $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Se}]$ is tetragonal, $\text{P}\bar{4}2_1\text{c}$, with $a = 14.984(5)$ Å and $c = 19.165(9)$ Å. For $Z = 4$ the calculated density is 1.491 g/cm³. The structure was refined by full-matrix least-squares to a conventional R factor of 0.031, [3797 data, $F^2 > 2\sigma(F^2)$]. The selenium atom is on a two-fold axis and bonds to two Yb atoms in a nearly linear structure (Yb-Se-Yb angle, $171.09(6)^\circ$). The Yb atom is η^5 -bonded to two cyclopentadienyl rings and is on a plane defined by the centers of the two rings and the selenium atom. Distances are: Yb-Se, $2.621(1)$ Å; Yb-C (ave), $2.609(7)$ Å; $\langle \text{Yb-Cp}(\text{ring}) \rangle$ $2.319(2)$ Å, and Yb-Se-Yb is $171.09(6)^\circ$.

The divalent lanthanide metallocene, $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$, has been shown to be an electron-transfer reagent towards a variety of organic and organo-transition metal compounds.¹ In these reactions $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ acts as a soluble source of an electron (the reduction potential of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ in acetonitrile is -1.35v (SCE)^{1d}) and the tight ion-pair complexes that result are often readily soluble in and crystallize from hydrocarbon solvents. The tight ion-pairs are of considerable interest since deductions about the electronic structure of the anionic fragments can be made from the solid state structure. In this way insight into the bonding in negative ions, radical anions, and dianions have been obtained. The electron-transfer chemistry of the trivalent uranium metallocene, $(\text{RC}_5\text{H}_4)_3\text{U}$, has been explored pair-wise with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and the results have been used in a similar way.² One of the most interesting structural features in the uranium studies is the reaction product of $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ and Ph_3PS , $[(\text{Me}_5\text{H}_4)_3\text{U}][\mu\text{-S}]$, in which the U-S-U angle is $164.9(5)^\circ$ and the U-S distance of $2.60(1)$ Å is the shortest U-S distance so far determined. There is no magnetic interaction in the chalcogenide-bridged complexes, $[(\text{MeC}_5\text{H}_4)_3\text{U}][\mu\text{-E}]$ where E is S, Se, or Te, since the magnetic susceptibility as a function of temperature (4-300K) shows that the $5f^2$ -ions behave as isolated paramagnets.^{2b} The related ytterbium(III) complexes, $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-E}]$, were of interest to see if the behavior patterns discovered in the 5f-series applied to the 4f-series.

In this paper we describe the series $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-E}]$ where E is O, S, Se, or Te, and the crystal structure of the selenium compound.

Results and Discussion

The bridging chalcogenides were prepared by reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ and R_3PE , where R is Ph or Bu^n and E is S, Se, or Te. The sulfide can be prepared by reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ with either COS or As_2S_3 , but not from elemental sulfur. The selenium and tellurium complexes can be prepared from the non-metals in their massive state with the metallocene in hydrocarbon solvent. The bridging oxide can be made from $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ and nitrous oxide in hexane, though the yield is low. A better synthetic method is to use base-free $(\text{Me}_5\text{C}_5)_2\text{Yb}$ rather than its diethyl ether complex.

Some physical properties are shown in Table I. The melting points monotonically decrease down the series as does the Yb-E-Yb stretching frequency in the infrared spectrum. The solubility in hydrocarbons is inversely related to the melting point, the oxide being only sparingly soluble whereas the telluride is very soluble in hexane. All the compounds give molecular ions in the mass spectrum and the molecules have substantial thermal stability. The trends in physical properties are similar to those found for the related tetravalent uranium compounds, $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-E}]^{2c}$. It is interesting to note that chemical shift of the Me_5C_5 -group in the ^1H NMR spectra moves downfield on going from oxygen to selenium then moves upfield on going to tellurium, and the width at half-height decreases substantially from oxygen to tellurium.

Magnetic susceptibility data for all of ytterbium compounds were measured as a function of temperature (4-280K) and these data are tabulated in Table II. A plot of the χ_M^{-1} vs. T(K) for the bridging

sulfide is shown in Figure I. All of the compounds prepared in this study give similar plots. The plots of χ_M^{-1} are similar in shape and the value of the effective magnetic moment are similar to other mononuclear compounds of the type $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{X})(\text{L})$ where X is an anionic-ligand and L is a neutral ligand^{1,3} and to the free-ion and its coordination compounds.⁴ This suggests that the extent of magnetic exchange between the $4f^{13}$ ions across the bridging ligand is very small or non-existent and the Yb(III) centers behave as independent paramagnets. A similar conclusion was reached about the U(IV) centers in $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-E}]$.^{2c} The plot of χ_M^{-1} vs. T from 5-35K follows the Curie-Weiss law with a small θ and μ is slightly lower than that found from 100-280K. The behavior in the high temperature regime also follows Curie-Weiss behavior with θ slightly larger than that found at lower temperature and the magnetic moment is ca. 4.4 B.M. for all of the complexes. For the free-ion the term symbol is $^2F_{7/2}$ and the magnetic moment is predicted to be 4.50 B.M. at 300K.⁴ The crystal field splitting, the values of which are on the order of kT ($kT = 208 \text{ cm}^{-1}$ at 300K), will remove the degeneracy of the $^2F_{7/2}$ state and as a consequence at temperatures less than 100K the slope of χ_M^{-1} vs. T changes as the population of the crystal field levels changes. The crystal field splittings cannot be specified more precisely due to the low symmetry of the complexes, but a rigorous analysis has been done for a Yb(III) complex in D_{3h} symmetry.^{5a}

With regards to magnetism studies of lanthanide ions with pentamethylcyclopentadienyl ligands, it was of interest to examine the behavior of $(\text{Me}_5\text{C}_5)_2\text{Sm}$ ^{6a} and $[(\text{Me}_5\text{C}_5)_2\text{Sm}]_2[\mu\text{-O}]$ ^{6b} as a function of

temperature since Sm(II) and Sm(III), f^6 and f^5 ions, respectively, have interesting magnetic properties as a function of temperature because the splitting of the free-ion energy levels is small relative to kT . This behavior has been termed anomalous by Van Vleck.^{4a} Trivalent europium compounds are the molecules usually studied as representative f^6 ions, though a trivalent, pentamethylcyclopentadienyl compound cannot be prepared since the Me_5C_5^- is too strongly reducing and the divalent complexes, $(\text{Me}_5\text{C}_5)_2\text{Eu(L)}$, are isolated from EuCl_3 .^{7a} The Eu(II) ion is a f^7 ion with term symbol ^8S . The plot of χ_M^{-1} vs. T for the base-free $(\text{Me}_5\text{C}_5)_2\text{Eu}^{7b}$ follows essentially Curie behavior from 5 to 280K since θ is near 0K at 5 and 40 kGauss with $\mu = 7.70$ and 7.84 B.M., respectively, close to the spin-only value of 7.94 B.M.

The anomalous magnetic behavior of Eu(III) and Sm(III) has been treated by Van Vleck for free-ions and applied to simple salts.^{4a} The anomaly is due to the fact that for the Eu(III) and Sm(II) free-ions of f^6 electron configuration with term symbol $^7\text{F}_0$, the separation of the $J = 0$ and $J = 1$ states is ca. 300 cm^{-1} and the separation of the $J = 1$ and $J = 2$ states is ca. 200 cm^{-1} , both of which are on the order of kT . Similarly for Sm(III), the free-ion ground state term symbol is $^6\text{H}_{5/2}$ and the $J = 5/2$ to $J = 7/2$ transition energy is ca. 900 cm^{-1} , again on the order of $3kT$. In contrast, in the free-ion Yb(III) the $J = 7/2$ to $J = 5/2$ transition energy is ca. $10,000 \text{ cm}^{-1}$, much larger than kT . When the separation of the ground state from the excited state or states is on the order of kT , complex behavior results. Plots of χ_M^{-1} vs. T for simple salts show that f^5 and f^6 ions show temperature independent paramagnetism (T.I.P.).⁴ The plot of χ_M^{-1} vs. T for $(\text{Me}_5\text{C}_5)_2\text{Sm}$ shown in

Figure IIa is similar to that found for $(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{thf})(\text{OEt}_2)$ and these are very similar to those found in simple europium(III) salts.⁴ The slope of χ_M^{-1} vs. T, when most of the electrons are in the ground state at low T, shows that χ_M is independent of temperature and as T increases the J = 1 and J = 2 states become populated so that at 300K, $\mu = 3.4$ to 3.5 B.M. according to Van Vleck. For $(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{thf})(\text{OEt}_2)$ at 40 kGauss the value of $\chi_M(\text{Corr})$ at 280.0K is 4.74×10^{-3} emu mol⁻¹ which gives $\mu(280.0\text{K})$ of 3.26 B.M. since $\mu = 2.828 (\chi_M T)^{1/2}$.⁸ For $(\text{Me}_5\text{C}_5)_2\text{Sm}$ at 5 kGauss the value of $\chi_M(\text{corr})$ at 281.7K is 5.016×10^{-3} emu mol⁻¹ and $\mu(281.7\text{K})$ is 3.36 B.M. At 40 kGauss $\chi_M(\text{corr})$ is 5.032×10^{-3} emu mol⁻¹ and $\mu(282.7\text{K})$ is 3.37 B.M. These solid state values are in good agreement with the literature values for $(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{thf})_2$ of $\chi_M(296\text{K}) = 5.490 \times 10^{-3}$ emu mol⁻¹ and $\mu(296\text{K}) = 3.6$ B.M.^{6c} and for $(\text{Me}_5\text{C}_5)_2\text{Sm}$ of $\chi_M(297\text{K}) = 5.70 \times 10^{-3}$ emu mol⁻¹ and $\mu(297\text{K}) = 3.7$ B.M.^{6a} as reported by Evans using the Evans' NMR method.

As stated above, Sm(III) shows temperature independent paramagnetism (T.I.P.) and $[(\text{Me}_5\text{C}_5)_2\text{Sm}]_2[\mu\text{-O}]$ illustrates this very well. The plot of χ_M^{-1} vs. T is shown in Figure IIb and it is similar to that observed for simple Sm(III), salts and explained by Van Vleck.⁴ The magnetic moment, evaluated at 300K is 1.53 B.M. per Sm(III) is close to that predicted by Van Vleck of 1.55 to 1.65 B.M. and found in solution by Evans of 1.8 B.M. at 298K.^{6b}

The detailed magnetic susceptibility studies of the pentamethylcyclopentadienyl complexes of the lanthanides reported here and elsewhere¹ are revealing relative to the nature of the metal-ring bonding. In the mononuclear compounds the observed shape of the χ_M^{-1}

vs. T plots and the value of μ shows that the crystal field splitting caused by the pentamethylcyclopentadienyl ligand is not very different from that caused by negatively charged ligands in simple salts or that of the free-ion. The small crystal field splitting due to the Me_5C_5^- ligand in the lanthanide complexes is in contrast to the high crystal field splitting caused by this ligand in d-transition metal chemistry.¹⁰ It is particularly noteworthy that $(\text{Me}_5\text{C}_5)_2\text{Mn}$ is a low spin complex in solid state and in gas phase,^{11a-c} whereas the $(\text{RC}_5\text{C}_4)_2\text{Mn}$ compounds are either high spin or spin equilibrium molecules.^{11d} The Me_5C_5^- ligand molecular orbitals do not interact (mix) with the lanthanide metal atomic orbitals as much as they do with the d-transition metal atomic orbitals and the crystal field splitting in the lanthanide metallocenes is small relative to that found in d-transition metallocenes. The small crystal field splitting is consistent with the widely held view that the 4f-transition metal to ligand bonds are rather more ionic than equivalent bonds in the d-transition metal series.^{12,7b} The orbital energy mismatch also rationalizes why the bridging complexes, $[(\text{Me}_5\text{C}_5)_2\text{M}]_2[\mu\text{-E}]$, do not show magnetic exchange coupling.

The principal structural features of interest in the bridging chalcogenide molecules were the angle at the chalcogenide atom and the metal-chalcogenide distance. The only complex that we have been able to get as X-ray quality crystals to date is the bridging selenide complex. An ORTEP diagram is shown in Figure III, positional parameters are in Table III, some bond lengths and angles are in Table IV, and crystal data are in Table V. The molecule lies on a crystallographic two-fold axis with a Yb-Se-Yb angle of $171.09(6)^\circ$. If the Yb-Se-Yb angle were

linear, then the molecule would have idealized S_4 -symmetry like the samarium complex $[(Me_5C_5)_2Sm]_2[\mu-O]$.^{6b} The averaged Yb-C distance is 2.609 ± 0.007 Å and the Yb-ring centroid distance is 2.32 Å, consistent with Yb(III) in seven coordination.^{1,11}

The Yb-Se distance is 2.621(1) Å. The only other ytterbium-selenium distances are 2.89 Å in $CdYb_2Se_4$ ^{12a} and 2.83 Å in Yb_2Se_3 ^{12b} in which each trivalent ytterbium is six coordinate. The Yb-Se distance in $[(Me_5C_5)_2Yb]_2[\mu-Se]$ is short by this comparison. Using $[(Me_5C_5)_2Sm]_2[\mu-O]$ as a reference and correcting the bond length for the change in bridging ligand¹³ and for the change in the identity of the metal atoms from Sm to Yb in seven coordinations¹⁴ predicts that the Yb-Se distance should be ca. 0.40 Å longer than the Sm-O distance. In fact the Yb-Se distance is 0.63 Å longer. Using the U-S distance in $[(MeC_5H_4)_3U]_2[\mu-S]$ ^{2c} as a reference and correcting the radius of tetravalent uranium in ten coordination for trivalent ytterbium in seven coordination¹⁴ and the radius of sulfur for selenium predicts that the Yb-Se distance should be 0.26 Å longer than the U-S distance whereas it is only 0.02 Å longer. Clearly the standard for shortness determines our operational definition of shortness or longness. As pointed out previously,^{2c} the near linear Yb-Se-Yb bond angle and the short Yb-Se bond length, as determined by comparison with Yb_2Se_3 or $Cd_2Yb_2S_4$, could imply Yb-Se π -bonding though the lack of magnetic interaction argues against appreciable covalent mixing. On the other hand the near linear Yb-Se-Yb geometry could be as bent as it can be; the intramolecular Me_5C_5 non-bonded repulsions preventing further bending and therefore hindering the development of the lone-pairs on the bridging selenide.

On the basis of the structural information that is currently available to us it is impossible to choose between these two extreme explanations. More structural information is desirable; we are trying to grow single crystals of the other chalcogenide molecules reported here.

Experimental Section

All reactions were done under nitrogen. Analyses were done by the microanalytical laboratory of this department. Infrared spectra were recorded as Nujol mulls with the use of a Nicolet 5DX-FTIR instrument. Proton NMR spectra were measured on a JEOL FX-90Q instrument operating at 89.56 MHz on solutions in C_6D_6 or C_7D_8 . Chemical shifts are expressed in δ -values with positive values to high frequency of tetramethylsilane. Magnetic susceptibility studies were done similar to those previously described.¹⁷ The mass spectra were recorded on a AEI-MS-9 instrument using electron impact ionization and are expressed as M^+ (observed intensity, calculated intensity).

$[(Me_5C_5)_2Yb]_2[\mu-O]$. Base-free $(Me_5C_5)_2Yb^{7b,18}$ (0.41g, 0.92 mmol) in pentane (40 mL) was treated with nitrous oxide (3 atm) in a heavy-walled pressure bottle for 4h. The pressure was released and the orange solution and precipitate was transferred to a Schlenk tube. The volume of the solution was reduced to ca. 5 mL and the solution was cooled to $-25^\circ C$ to effect complete precipitation. The solid was collected and then crystallized from a minimum amount of hot toluene as orange crystals in 55% (0.23g) yield. Anal. Calcd for $C_{40}H_{60}OYb_2$: C, 53.2; H, 6.70. Found: C, 52.7; H, 6.78. IR: 2728w, 1650w, 1497m, 1302w, 1168sh,

1154w, 1133sh, 1024m, 957w, 895sh, 863w, 756w, 735sh, 724w, 695m, 673s, 641w, 625m, 593w, 566w, 478w, 432sh, 384mbr, 309sh, 301vsbr, 283sh cm^{-1} . MS: M^+ , 897 (11.9, 3.82); 898 (20.2, 15.1); 899 (44.0, 34.6); 900 (45.2, 58.3); 901 (61.3, 85.5); 902 (100, 100); 903 (78.6, 90.9); 904 (87.5, 92.4); 905 (46.4, 49.5); 906 (25.0, 45.3); 907 (19.0, 16.5); 908 (11.3, 9.70). Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ with N_2O in hydrocarbon solution gives a low yield (18%) of the bridging oxide.

$[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-S}]$. An intimate mixture of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ (0.81g, 1.6 mmol) and Ph_3PS (0.23g, 0.78 mmol) was dissolved in toluene (60 mL) and the red solution was refluxed for 5h. After cooling to room temperature the red solution was concentrated to ca. 20 mL and cooled to -20°C . The sulfide was isolated as deep red needles by filtration in 49% yield (0.35 g). Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{SYb}_2$: C, 52.3; H, 6.58; S, 3.49. Found: C, 53.6; H, 6.71; S, 3.44. IR: 2725m, 1492m, 1256m, 1212m, 1152w, 1092m, 1064w, 1022m, 800w, 728s, 694w, 666m, 638w, 588w, 517w, 482w, 462w, 379vs 310vs cm^{-1} . MS: M^+ , 914 (9.0, 15.0); 915 (36, 34); 916 (61, 57); 917 (91, 85); 918 (100, 100); 919 (97, 92); 920 (96, 94); 921 (55, 52); 922 (50, 48); 923 (20, 18). The bridging sulfide can also be prepared from $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ and As_2S_3 in hexane in 51% yield or with carbonylsulfide in diethyl ether in 17% yield. In each case the isolated material was identified by mp and IR.

$[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Se}]$. An intimate mixture of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ (0.67g, 1.3 mmol) and $\text{Ph}_3\text{PSe}^{19}$ (0.22g, 0.65 mmol) was stirred in hexane (70 mL) for 1hr. The purple solution was filtered and the filtrate was

concentrated to ca. 15 mL. Cooling the filtrate to -25°C for 2 days afforded purple crystals which were collected and dried under reduced pressure in 64% (0.40g) yield. Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{SeYb}_2$: C, 49.7; H, 6.26. Found: C, 49.9; H, 6.49. The infrared spectrum is essentially superimposable on that of the bridging sulfide spectrum with exception of the bands at 379 and 247 cm^{-1} . MS: M^+ ; 959 (9, 7); 960 (16, 15); 961 (33, 27); 962 (50, 44); 963 (76, 64); 964 (84, 82); 965 (100, 93); 966 (92, 100); 967 (70, 82); 968 (56, 80); 969 (31, 45); 970 (15, 40); 971 (8, 16). The bridging selenide can also be prepared by stirring $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ with selenium metal in hexane for 12h in 66% isolated yield.

$[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Te}]$. Tri-n-butylphosphinetelluride²⁰ (0.37g, 1.1 mmol) in hexane (45 mL) at -30°C was added to $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ (1.2g, 2.2 mmol) in hexane (80 mL) at room temperature and the blue-green solution was stirred for 1h. The solution was filtered, the filtrate was concentrated to ca. 20 mL and cooled (-20°C) for several days to give black-green crystals, 0.47g (41% yield), which were collected and dried under reduced pressure. Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{TeYb}_2$: C, 47.4; H, 5.96. Found: C, 48.4; H, 6.37. The infrared spectrum was essentially identical to that of the bridging sulfide except for the absorption at 379 cm^{-1} in the latter compound. MS: M^+ , 1008 (14, 11); 1009 (22, 21); 1010 (33, 36); 1011 (54, 53); 1012 (76, 71); 1013 (85, 87); 1014 (92, 100); 1015 (100, 96); 1016 (97, 99); 1017 (67, 68); 1018 (63, 65); 1019 (32, 31); 1020 (19, 25). The bridging telluride may be prepared by

stirring $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ and an excess of tellurium metal in hexane for 3 days in 54% isolated yield.

$(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{OEt}_2)(\text{thf})$. A solution of NaC_5Me_5 (1.73g, 10.9 mmol) in tetrahydrofuran (50 mL) was added to $\text{SmI}_2(\text{thf})_2^{21}$ (3.00g, 5.47 mmol) in tetrahydrofuran (80 mL) and the brown-red suspension was stirred for 1h. The solution was filtered and the filtrate was evaporated to dryness. The residue was extracted with diethyl ether (50 mL) and the brown solution again was evaporated to dryness. The brown residue was redissolved in diethyl ether (25 mL) and the solution was concentrated to incipient crystallization, then cooled to -25°C . The brown prisms were collected and dried under reduced pressure. The mother liquor gave a second crop of crystals in a combined yield of 78% (2.1g), mp $134-137^\circ\text{C}$. A sample of the complex was dissolved in benzene- d_6 and then hydrolyzed with water. The ^1H NMR spectrum of the benzene solution contained equal amounts of diethyl ether and tetrahydrofuran. ^1H NMR (C_7D_8 , 32°C): δ 16.03, 4H ($\nu_{1/2} = 16$ Hz); 10.99, t, $J = 6.6$ Hz, 6H; 2.98, 30H ($\nu_{1/2} = 2$ Hz); 2.52, 4H ($\nu_{1/2} = 11$ Hz); -0.59, q, $J = 6.6$ Hz, 4H. IR: 2720m, 1148m, 1120w, 1080s, 1061m, 1035s, 1009w, 949w, 932w, 897vs, 838w, 797w, 725w, 258vs cm^{-1} .

$(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{thf})$. The mixed diethyl ether, tetrahydrofuran complex prepared above (0.30g, 0.53 mmol) was dissolved in toluene (30 mL) and stirred for 1h, then the brown solution was warmed to 45°C and the toluene was removed under reduced pressure to yield a green residue. The residue was dissolved in hexane and the now brown-red solution was

filtered and the filtrate was concentrated to ca. 10 mL and cooled (-25°C). The large green-brown needles (0.25 g, 96% yield) were collected and dried under reduced pressure, mp 155-157°C. Anal. Calcd for $C_{24}H_{38}OSm$; C, 58.5; H, 7.77. Found: C, 58.1; H, 7.75. A sample of the compound was dissolved in benzene- d_6 and then hydrolyzed with water. The 1H NMR spectrum of the benzene phase showed resonances due to tetrahydrofuran and no resonances due to diethyl ether. 1H NMR (C_7D_8 , 32°C): δ 11.94, 4H($\nu_{1/2}$ = 29Hz); 3.73, 30H($\nu_{1/2}$ = 2Hz); -0.11, 4H($\nu_{1/2}$ = 12Hz). IR: 2720m, 1307w, 1255m, 1208w, 1150m, 1084s, 1031w, 977w, 945m, 890sbr, 800s, 726vs 610w, 576w, 350mbr, 280vs cm^{-1} .

(Me $_5$ C $_5$) $_2$ Sm(OEt) $_2$. Samarium diiodide bis(tetrahydrofuran) was ground into a fine powder and heated under reduced pressure at 160°C for 16h. During this time the color changed from blue-grey to deep green. The green material was shown to be essentially free of tetrahydrofuran by a very thick Nujol mull infrared spectrum. The base-free SmI_2 (4.34g, 10.7 mmol) and NaC_5Me_5 (3.17g, 20.0 mmol) in diethyl ether (250 mL) were stirred for 17h. The brown-green solution was filtered and the volume of the filtrate was reduced to ca. 125 mL. Cooling (-15°C) yielded large deep green needles. Two additional crops of crystals were harvested from the mother liquor giving a combined yield of 3.6g (73%), mp 190-192°C. Anal. Calcd for $C_{24}H_{40}OSm$: C, 58.2; H, 8.15. Found: C, 58.0; H, 8.20. A sample of the complex was hydrolyzed in C_6D_6 with D_2O . Examination of the C_6D_6 layer by 1H NMR spectroscopy showed resonances due to diethyl ether and $(Me_5C_5)D$ in a 1:1 ratio. 1H NMR (C_7D_8 , 31°C): δ 20.73, 6H, t, J = 6 Hz; 2.77, 30H ($\nu_{1/2}$ = 4 Hz; -4.50, 4H, q, J =

6 Hz. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , -30°C): δ 136 (OCH_2Me), 102.6 (C_5Me_5), 94.94 (OCH_2Me), -137.9 (C_5Me_5). The methylene carbon resonance of the diethyl ether could not be observed at 30°C as it overlapped with the aryl resonances of C_6D_6 . IR: 2723m, 1468m, 1164m, 1145s, 1080vs, 1038s, 1018m, 929m, 837s, 818w, 799w, 774w, 731w, 635w, 611m, 589w, 443w, 364mbr, 307m, 268sbr cm^{-1} . This complex has been characterized by a single crystal X-ray crystallographic study.²²

$(\text{Me}_5\text{C}_5)_2\text{Sm}$. The diethyl ether complex (3.9g, 7.8 mmol) was dissolved in toluene (200 mL) and the deep green solution was heated to 100°C and the solvent was slowly removed (ca. 2h) under reduced pressure. The residue was dissolved in an additional 100 mL of toluene and the "toluene reflux" was repeated. The green residue was dissolved in toluene (200 mL), filtered, and the filtrate was concentrated to ca. 120 mL. Cooling to -25°C gave large brown-green blocks. Two additional crops of crystals were obtained from the mother liquor in a combined yield of 2.7 (80%), mp $214\text{--}217^\circ\text{C}$. The compound sublimed at $120\text{--}130^\circ\text{C}/10^{-3}$ mm. A sample of the compound was hydrolyzed with water in C_6D_6 and examination of the hydrolysate by ^1H NMR spectroscopy showed no diethyl ether resonances. The IR and ^1H NMR spectra were identical to those previously reported,^{6a,d} though the region below 800 cm^{-1} was not measured. IR: 2712w, 1649wbr, 1577vw, 1497w, 1436s, 1162w, 1146w, 1058w, 1018w, 950w, 721w, 656w, 628w, 602w, 557w, 477w, 372sh, 359m, 299sh, 268s cm^{-1} . MS: M^+ , 414 (12, 12); 415 (2.5, 2.6); 417 (62, 56); 418 (55, 55); 419 (60, 63); 420 (37, 40); 421 (8.8, 7.4); 422 (100, 100); 423 (26, 23); 424 (79, 87); 425 (16, 19); 426 (1.4, 2.0). Higher

mass peaks due to $(\text{Me}_5\text{C}_5)_2\text{Sm}_2$ and $(\text{Me}_5\text{C}_5)_3\text{Sm}_2$ ions are observed in variable abundances though always in small to moderate amounts relative to M^+ .

$(\text{Me}_5\text{C}_5)_2\text{Sm}[\mu\text{-O}]$. Base-free $(\text{Me}_5\text{C}_5)_2\text{Sm}$ (0.31g, 0.74 mmol) was dissolved in toluene (30 mL) and the solution was transferred to a thick-walled pressure bottle and the bottle was pressurized to 3 atm with N_2O . The color of the solution changed from green to yellow and the solution was stirred for 6h. The solution was transferred to a Schlenk flask and the volume of the solution was reduced to ca. 10 mL. Cooling afforded yellow flakes. A second crop of crystals was obtained from the mother liquor in a combined yield of 60% (0.19g). The ^1H NMR spectrum was identical to that previously reported.^{6b} The mass spectrum does not show a M^+ , but a $\text{M-C}_5\text{Me}_5^+$ envelope is observed. The bridging oxide can also be prepared from $(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{OEt}_2)$ and N_2O in toluene in 43% yield.

$(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{OEt}_2)$. Europium diiodide, prepared as described in ref. 23 or by heating $\text{EuI}_2(\text{thf})_2$ ²¹ at 180°C for 15h under reduced pressure, (2.7g, 6.7 mmol) and NaC_5Me_5 (2.0g, 13 mmol) were stirred in diethylether (150 mL) for 17h. The solution was filtered and the volume of the filtrate was reduced to ca. 180 mL; cooling (-25°C) gave dark red crystals which were collected and dried under reduced pressure. A second crop of crystals was obtained from the mother liquor in a combined yield of 2.2g (69%), mp 192-195°C. Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{OEu}$: C, 58.1; H, 8.12. Found: C, 57.9; H, 8.07. IR: 2721w, 1488w, 1284m,

1163w, 1144s, 1079s, 1037s, 1017m, 929m, 838s, 819w, 797m, 590m, 551w, 442w, 358s, 270s cm^{-1} . A sample of the complex in C_6D_6 was hydrolyzed with D_2O . Examination of the benzene extract by ^1H NMR spectroscopy showed that diethyl ether and $\text{C}_5\text{Me}_5\text{D}$ were present in a 1:2 ratio. The single crystal X-ray structure of this complex has been done.²²

$(\text{Me}_5\text{C}_5)_2\text{Eu}$. The europium diethyl ether complex (2.2g, 4.4 mmol) was dissolved in toluene (200 mL) and the orange-red solution was heated to 100°C and the toluene was removed slowly under reduced pressure (2-3h) in a grease-less Schlenk flask. The residue was dissolved in toluene (200 mL) and the solvent was removed as before. The orange residue was dissolved in hexane (250 mL), the volume was reduced to ca. 180 mL, cooling to -25°C afforded a total of two additional crops of crystals in a total yield of 1.6g (87%), mp $219-222^\circ\text{C}$. The complex sublimed at $120-130^\circ/10^{-3}$ mm. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{Eu}$: C, 56.9; H, 7.17. Found: C, 55.1; H, 7.18. A sample of the compound in C_6D_6 was hydrolyzed with D_2O . Examination of the benzene extract by ^1H NMR showed resonances due to $\text{C}_5\text{Me}_5\text{D}$ only. IR: 2725w, 1647w, 1494m, 1434vs, 1160w, 1149sh, 1017s, 948w, 720w, 628w, 602w, 584w, 569sh, 547w, 478wbr, 398sh, 364sh, 351m, 263vsbr cm^{-1} . MS: M^+ , 421 (90.5, 89.6); 422 (10.6, 20.0); 423 (100, 100); 424 (11.8, 22.0). This compound has been studied by single crystal X-ray crystallography.^{6d} In an attempt to get base-free $(\text{Me}_5\text{C}_5)_2\text{Eu}$, the "toluene-reflux" method was applied to $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{thf})(\text{OEt}_2)$.^{7a} The mono-tetrahydrofuran complex, $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{thf})$ ^{7a} was isolated as shown by mp and ir.

X-Ray Crystallography of $[(Me_5C_5)_2Yb]_2[\mu-Se]$

Purple air-sensitive crystals were sealed inside quartz capillaries in an argon filled drybox. X-ray diffraction intensities (θ - 2θ scans) were obtained using a modified Picker FACS-I automatic diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were corrected for absorption (analytical method), crystal decay and Lorentz and polarization effects. Experimental details of the data collection are tabulated in Table V. The ytterbium position was deduced from three-dimensional Patterson maps, and subsequent least-squares refinements and electron density maps revealed the rest of the non-hydrogen positions. Positional and anisotropic thermal parameters were refined by full-matrix least-squares; hydrogen atoms were not included. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.²⁴ Statistical results and other details of the least-squares refinements are tabulated in Table V.

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Supplementary Material Available. Thermal parameters, additional distances and angles, least-squares planes, and structure factor tables (21 pages).

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- (8) Using the slope of $\chi_M(\text{corr})^{-1}$ vs. T from T = 100 to 280K to calculate the magnetic moment, since $\chi_M = C(T-\theta)^{-1}$ and $\mu = 2.828C^{1/2}$, gives $\mu = 3.76$ B.M. and $\theta = -93\text{K}$ for $(\text{Me}_5\text{C}_5)_2\text{Sm}(\text{thf})(\text{OEt}_2)$ and $\mu = 3.84$ B.M. and $\theta = -84\text{K}$ for $(\text{Me}_5\text{C}_5)_2\text{Sm}$, at 40kGauss.
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Figure Captions

- Figure 1. Plot of $\chi_M(\text{corr})^{-1}$ vs. T(K) for $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-S}]$.
- Figure II. Plot of $\chi_M(\text{corr})^{-1}$ vs. T(K) for (a) $(\text{Me}_5\text{C}_5)_2\text{Sm}$ and (b) $[(\text{Me}_5\text{C}_5)_2\text{Sm}]_2[\mu\text{-O}]$.
- Figure III. ORTEP drawing of $(\text{Me}_5\text{C}_5)_2\text{Yb}]_2[\mu\text{-Se}]$ viewed down a line connecting the centroids of the rings; thermal ellipsoids are at 50% probability level.

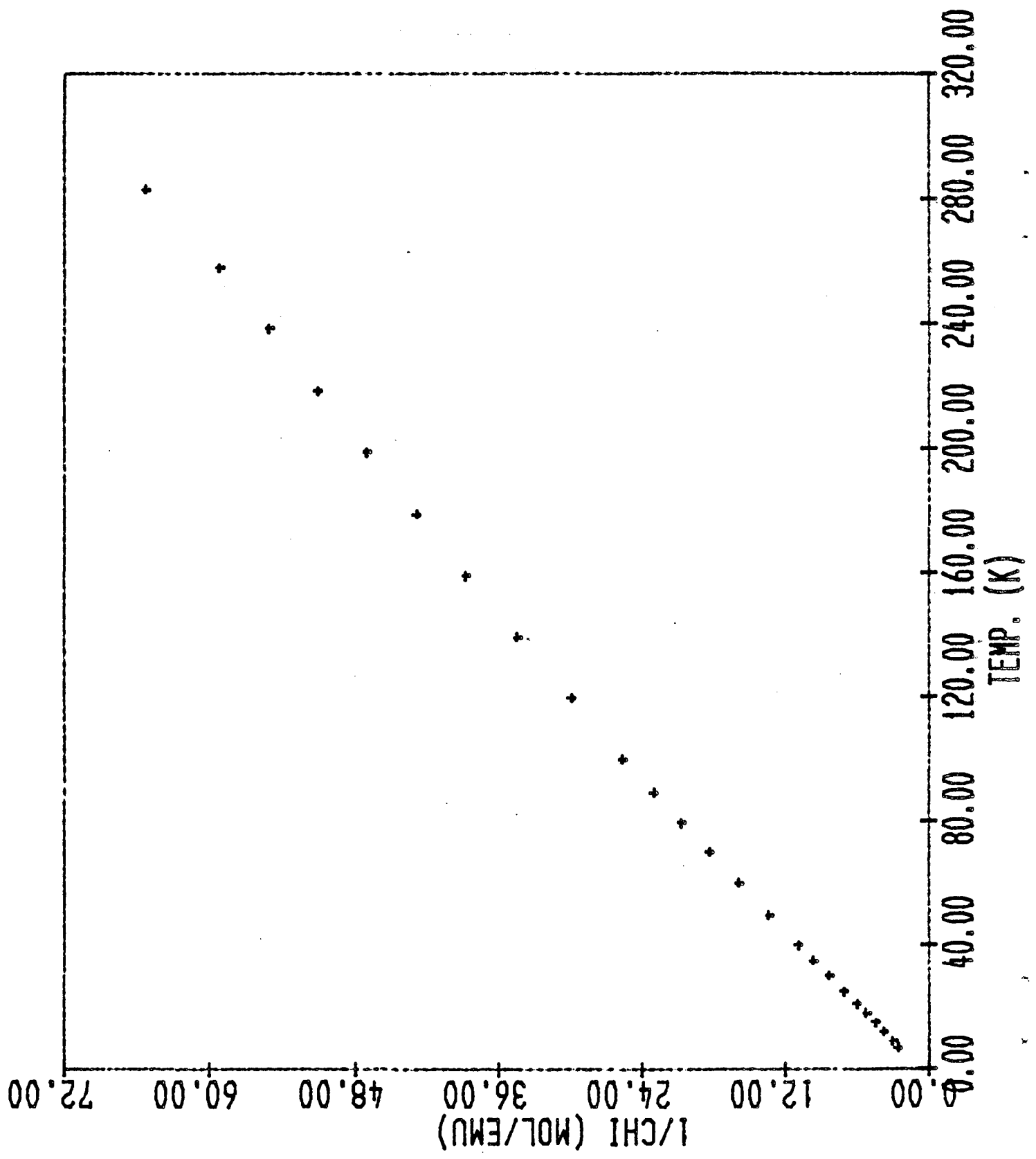


Figure 1

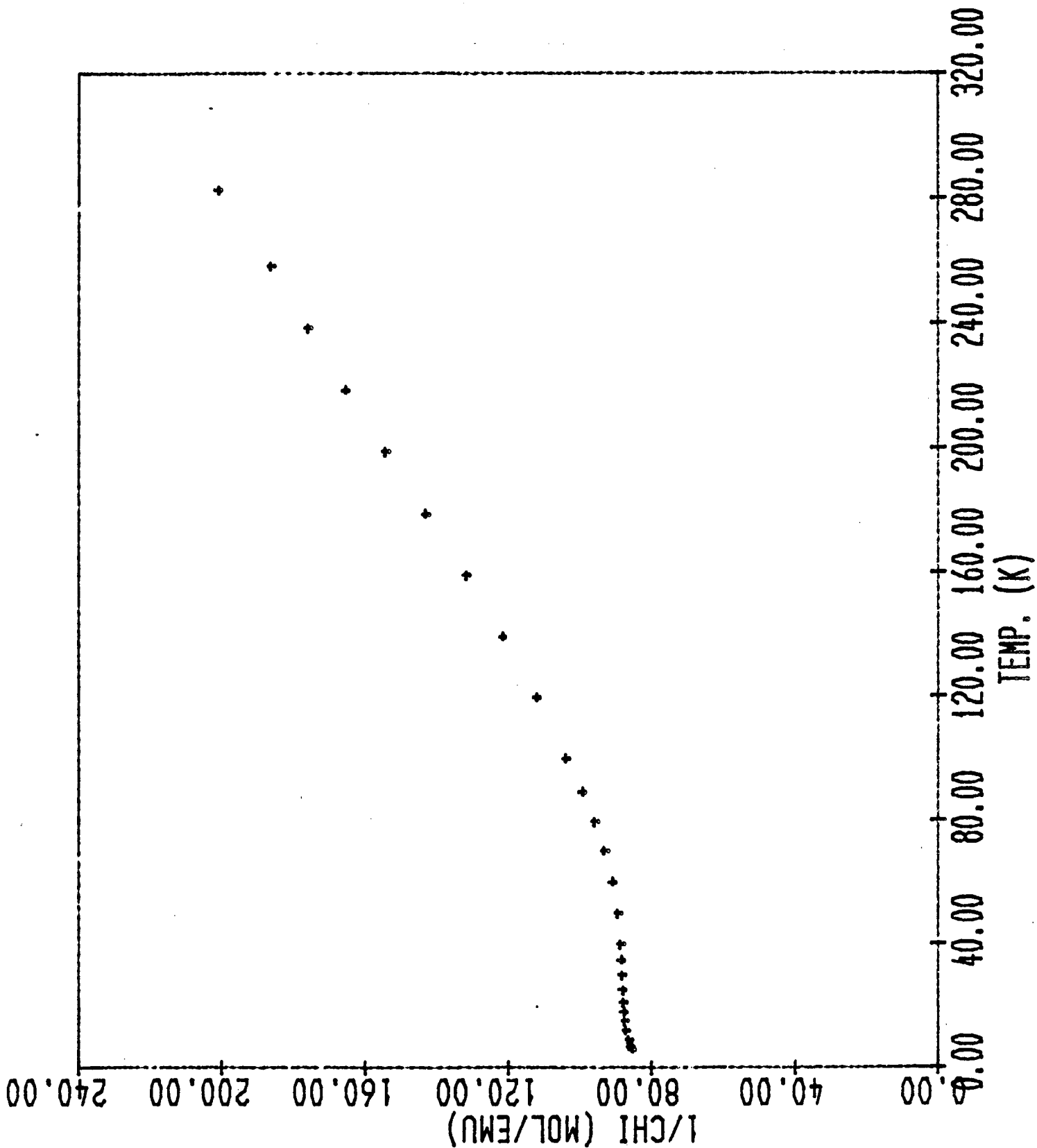


Figure 2 a

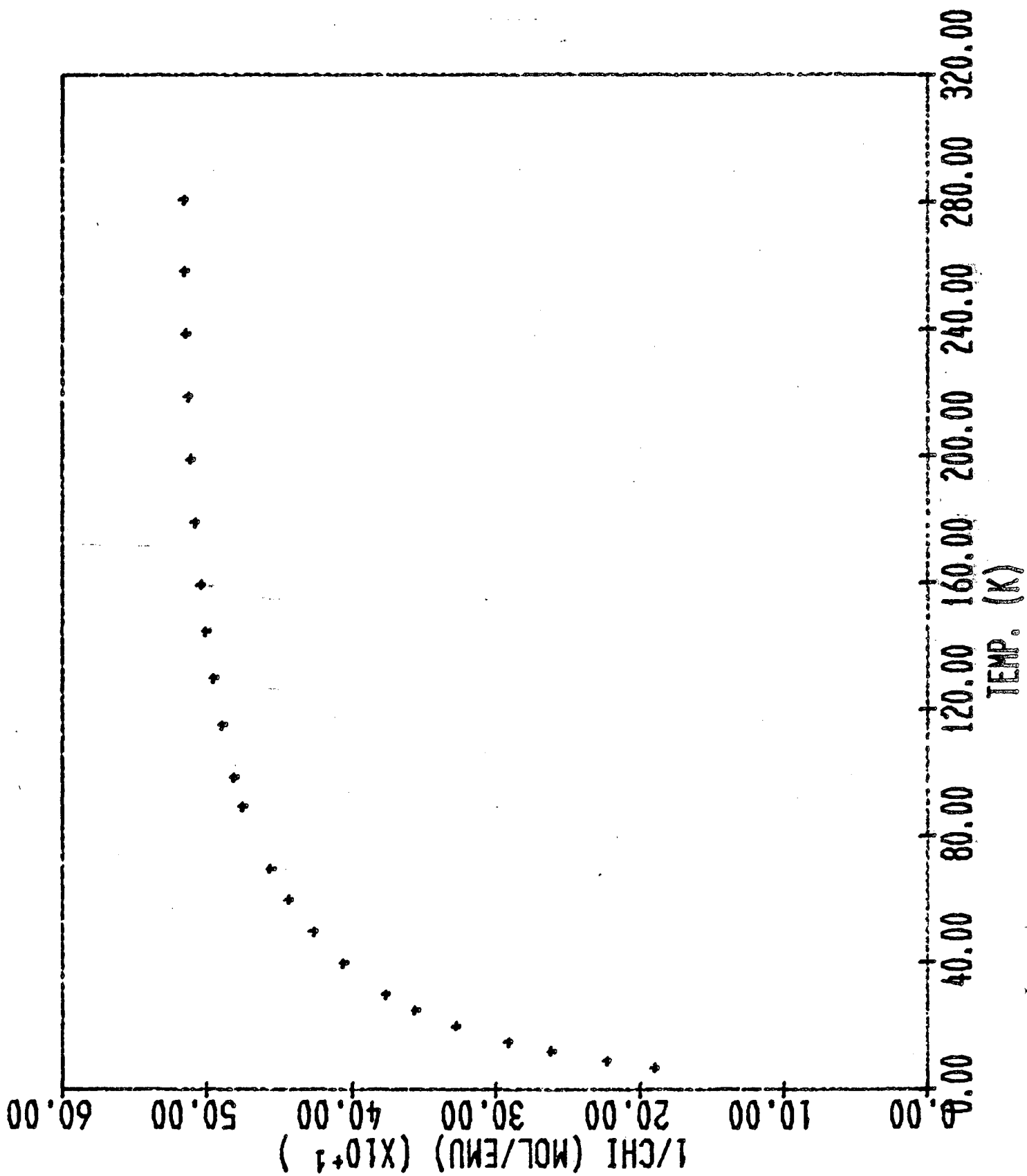


Figure 2b

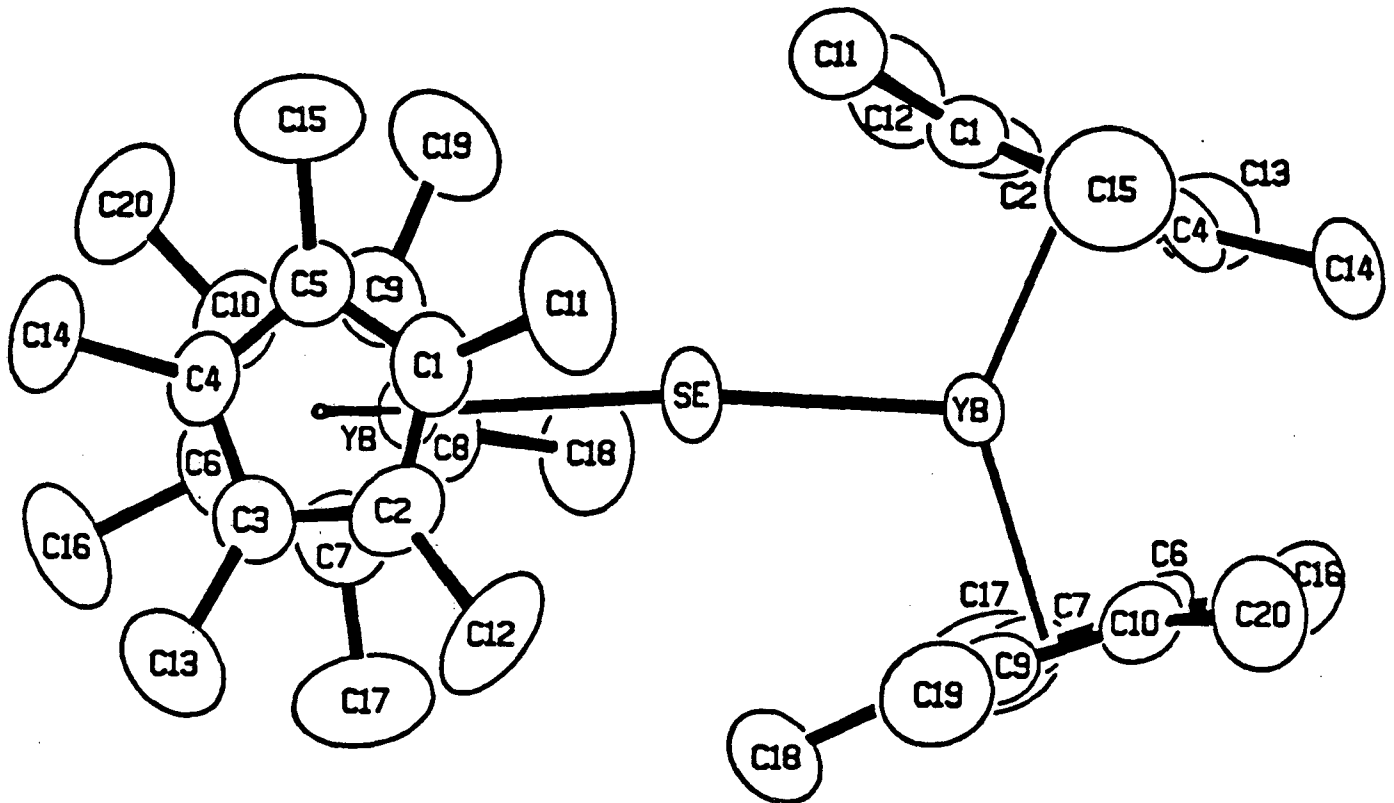


Figure 3

Table I.

Some Physical Properties of $[(Me_5C_5)_2Yb]_2[\mu-E]$

E	M.p.(°C)	Color	$\nu_{Yb-E-Yb}(cm^{-1})^a$	1H NMR ($\nu_{1/2}$) ^b
O	334-337	orange	673	24.4(980)
S	278-282	red	379	13.4(640)
Se	265-270	purple	247	12.1(500)
Te	235-238	green	-	12.6(290)

^aThe asymmetric stretching frequency, assuming a linear molecule, in the infrared spectrum. The assignment is made by comparison of the individual spectra. The band is of strong intensity.

^bThe 1H NMR spectrum in toluene- d_8 at 32°C; the chemical shift is expressed in δ -units and the width at half-height expressed in Hertz.

Table II.

Magnetic Susceptibility Studies on $[(Me_5C_5)_2Yb]_2[\mu-E]$

E	6-35K		100-280K	
	μ^a	θ^b	μ	θ
O	4.07	-2	4.31	-14
S	3.86	-2	4.32	-23
Se	4.14	-1	4.45	-15
Te	4.20	-2	4.42	-10

^aThe magnetic moment, μ , is calculated as $\mu = 2.828 C^{1/2}$ where C, the Curie constant, is the reciprocal slope from the plot of $[\chi_M(\text{corr})]^{-1}$ vs. T. Moments are expressed in Bohr magnetons per Yb(III). The values of μ and θ are averaged over two field strengths (5 and 40 kGauss). The $\chi_M(\text{corr})$ values are corrected for container and sample diamagnetism.

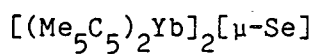
^bin degrees Kelvin.

Table III. Positional and Thermal Parameters with Estimated Standard deviations for $[\text{Me}_5\text{C}_5]_2\text{Yb}[\mu\text{-Se}]$

Atom	x	y	z	$B_{\text{eq}} \frac{a}{\text{\AA}}$
Yb	0.04694(2)	0.33203(2)	0.15232(2)	3.266(6)
Se	0	1/2	0.14169(6)	4.85(3)
C(1)	-0.0506(6)	0.3107(5)	0.0406(4)	4.9(2)
C(2)	-0.1001(5)	0.2757(6)	0.0958(4)	4.9(2)
C(3)	-0.0561(5)	0.1980(5)	0.1196(4)	4.5(2)
C(4)	0.0212(5)	0.1870(4)	0.0792(4)	4.6(2)
C(5)	0.0254(6)	0.2569(5)	0.0314(4)	4.6(2)
C(6)	0.1364(5)	0.2381(5)	0.2434(5)	4.9(2)
C(7)	0.1027(6)	0.3127(6)	0.2805(4)	5.1(2)
C(8)	0.1468(6)	0.3893(5)	0.2551(4)	4.8(2)
C(9)	0.2049(6)	0.3652(6)	0.2033(5)	5.2(2)
C(10)	0.1998(5)	0.2691(6)	0.1955(5)	5.3(2)
C(11)	-0.0800(11)	0.3876(8)	-0.0077(7)	8.5(4)
C(12)	-0.1896(7)	0.3104(8)	0.1199(8)	8.6(4)
C(13)	-0.0951(8)	0.1354(7)	0.1757(6)	7.2(3)
C(14)	0.0816(7)	0.1036(6)	0.0776(6)	6.5(3)
C(15)	0.0967(10)	0.2681(11)	-0.0249(7)	9.1(5)
C(16)	0.1213(8)	0.1390(7)	0.2630(7)	7.6(3)
C(17)	0.0366(8)	0.3086(12)	0.3413(7)	9.1(4)
C(18)	0.1414(9)	0.4835(8)	0.2874(6)	7.5(3)
C(19)	0.2677(8)	0.4245(8)	0.1595(8)	8.0(4)
C(20)	0.2642(7)	0.2145(7)	0.1517(8)	8.5(4)

$$\bar{a} B_{eq} = 1/3 \sum_{ij} B_{ij} a_i^* a_j^* a_i \cdot a_j$$

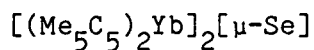
Table IV. Selected Distances (Å) and Angles (°) in



Yb	-	Cp(1) ^a	2.317		
Yb	-	Cp(2)	2.321		
Yb	-	Se	2.621(1)		
Yb	-	C(1)	2.612(7)		
Yb	-	C(2)	2.596(7)		
Yb	-	C(3)	2.610(6)		
Yb	-	C(4)	2.615(6)		
Yb	-	C(5)	2.596(7)		
Yb	-	C(6)	2.613(7)		
Yb	-	C(7)	2.611(7)		
Yb	-	C(8)	2.618(7)		
Yb	-	C(9)	2.608(8)		
Yb	-	C(10)	2.612(7)		
<C(Cp)	-	C(Cp)>	1.406(21)		
<C(Cp)	-	C(Me)>	1.535(12)		
Yb	-	Se	-	Yb	171.09(6)
Cp(1)	-	Yb	-	Se	110.39
Cp(2)	-	Yb	-	Se	110.63
Cp(1)	-	Yb	-	Cp(2)	138.94

^a Cp(1) and Cp(2) are the centroids of atoms C(1)-C(5) and C(6)-C(10) respectively.

Table V. Crystallographic Summary and Data Processing for



a, Å ^a	14.984(5)
c, Å	19.165(9)
cryst syst	tetragonal
space group	$P\bar{4}2_1c$
volume, Å ³	4302.9
d(calcd), g/cm ³	1.491
Z	4
temp (°C)	23.0
empirical formula	C ₄₀ H ₆₀ Se ₁ Yb ₂
f(000), e ⁻	1896
fw	965.96
wave-length (Kα ₁ , Kα ₂), Å	0.70930, 0.71359
crystal size (mm)	0.30x0.30x0.72
abs coeff, cm ⁻¹	51.68
abs corr range	3.30-4.28
cryst decay corr range	0.97-1.13
2θ limits, °	14.7-55.1
hkl limits	h 0, 19; k 0, 19; l -24, 19
scan width, °	1.20 + 0.693 × tanθ
no. of standards	3
no. reflections between stds	250
variation of standards (%)	3.44, 2.60, 2.46
no. scan data	9998
no. unique reflections	4830

Table V. (continued)

$R_{\text{int}}^{\text{b}}$	0.033
no. non-zero weighted data	3797 ($F^2 > 2\sigma$)
p^{c}	0.060
extinction k^{d}	5.91×10^{-8}
max % extinction corr	8.1 %
no. parameters	195
R (non-zero wtd dat) ^e	0.031
R_{w}^{f}	0.039
R (all data)	0.048
Goodness of fit ^g	1.00
max shift/esd in least-square	0.0027
max/min in diff map ($e/\text{\AA}^3$)	0.96, -0.67

^a Unit cell parameters from a least-squares fit to the setting angles of the unresolved MoK α components of 32 reflections ($21^\circ < 2\theta < 36^\circ$).

^b R_{int} = agreement factor between equivalent or multiply measured reflections
 $= \Sigma [I_{\text{hkl}} - \langle I_{\text{hkl}} \rangle] / \Sigma \langle I_{\text{hkl}} \rangle$

^c The assigned weights to F, $1.0/[\sigma(F)]^2$, derived from $\sigma(F^2) = [S^2 + (pF^2)^2]$, where S^2 is the variance of counting statistics and p is an empirical value that results in the weighted residuals of the strong and weak reflection being comparable.

^d Simple extinction correction, $F_{\text{obs}}(\text{corr}) = (1 + kI)F_{\text{obs}}$, where I is the uncorrected intensity and F_{obs} is the observed scattering amplitude

^e $R = \Sigma (|F_{\text{obs}}| - |F_{\text{cal}}|) / \Sigma |F_{\text{obs}}|$

Table V. (continued)

$$\frac{f}{R_w} = \sqrt{[\Sigma w(|F_{obs}| - |F_{cal}|)^2 / \Sigma w F_{obs}^2]}$$

$$\frac{g}{\sigma_1} = \text{error in observation of unit weight} = \sqrt{[\Sigma (w(|F_{obs}| - |F_{cal}|)^2) / (n_o - n_v)]},$$

where n_o is the number of observations and n_v is the number of variables.

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