

## SUPPORTING INFORMATION

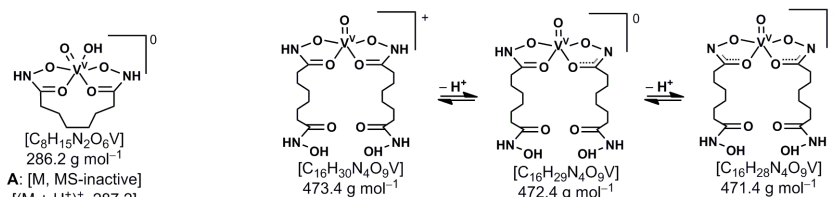
### Complexes Formed in Solution Between Vanadium(IV)/(V) and the Cyclic Dihydroxamic Acid Putrebactin or Linear Suberodihydroxamic Acid. Amalie A. H. Pakchung, Cho Zin Soe, Tulip Lifa, Rachel Codd

**Table S1.** Peaks from positive and negative ion mode ESI-MS spectra ( $m/z$  from 180 to 900) from solutions of V(IV) and sbhaH<sub>4</sub> ([V(IV)]:[sbhaH<sub>4</sub>] = 1:2 or 1:1) in 1:1 H<sub>2</sub>O:MeOH at pH values 2, 5, 7 and 9. Spectral acquisition repeated from different solutions (data from one series shown). The peak threshold was set at 3 or 6 for the positive- or negative-ion mode data, respectively.

| Positive ion mode |               |               |               |               |               |               |               |               |               | Negative ion mode |               |               |               |               |               |        |       |       |       |
|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|-------------------|---------------|---------------|---------------|---------------|---------------|--------|-------|-------|-------|
| pH 2              |               | pH 5          |               | pH 7          |               | pH 9          |               | pH 2          |               | pH 5              |               | pH 7          |               | pH 9          |               |        |       |       |       |
| V(IV):L = 1:2     | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 | V(IV):L = 1:2     | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 | V(IV):L = 1:2 | V(IV):L = 1:1 |        |       |       |       |
| $m/z$             | Rel %         | $m/z$         | Rel %         | $m/z$         | Rel %         | $m/z$         | Rel %         | $m/z$         | Rel %         | $m/z$             | Rel %         | $m/z$         | Rel %         | $m/z$         | Rel %         | $m/z$  | Rel % | $m/z$ | Rel % |
| 268.53            | 6.96          | 204.67        | 6.72          | 268.73        | 4.28          | 188.53        | 4.41          | 188.67        | 6.64          | 194.13            | 11.19         | 194.8         | 52.42         | 194.8         | 78.85         | 187.93 | 10.36 |       |       |
| 268.73            | 7.37          | 268.6         | 6.85          | 286.47        | 3.22          | 188.73        | 4.46          | 203.67        | 4.85          | 194.87            | 85.13         | 210.73        | 34.6          | 203           | 28.84         | 194.87 | 69.53 |       |       |
| 285.27            | 3.43          | 283.53        | 13.21         | 300.53        | 100.00        | 203.73        | 4.67          | 204.67        | 38.97         | 196.73            | 7.82          | 226.73        | 100           | 210.6         | 10.7          | 202.93 | 42.01 |       |       |
| 299.4             | 6.52          | 285.53        | 5.83          | 301.53        | 11.65         | 204.67        | 37.92         | 205.60        | 3.56          | 196.93            | 7.32          | 259.67        | 7.66          | 226.67        | 100           | 210.6  | 9.65  |       |       |
| 300.4             | 100           | 300.53        | 100           | 536.87        | 6.26          | 205.73        | 4.08          | 268.73        | 3.38          | 210.6             | 52.89         | 259.87        | 10.66         | 227.73        | 8.47          | 210.8  | 9.27  |       |       |
| 301.4             | 13.05         | 301.47        | 10.66         | 537.80        | 4.61          | 268.8         | 3.48          | 286.47        | 3.06          | 226.67            | 100           | 266.87        | 6.15          | 238.93        | 16.51         | 226.73 | 100   |       |       |
| 309.47            | 3.14          | 315.33        | 3.36          | 568.87        | 12.07         | 286.4         | 3.13          | 300.53        | 100.00        | 227.67            | 6.94          | 364.93        | 7.45          | 240.87        | 8.65          | 227.8  | 10.83 |       |       |
| 341.47            | 14.27         | 398.6         | 4.09          |               |               | 300.53        | 100           | 301.47        | 10.04         | 238.47            | 9.96          | 534.93        | 6.31          | 248.8         | 17.13         | 239    | 12.39 |       |       |
| 342.53            | 13.32         | 455.73        | 6.35          |               |               | 301.6         | 10.52         | 337.60        | 20.35         | 238.73            | 14.47         | 633.07        | 50.4          | 267           | 46.86         | 240.67 | 7.62  |       |       |
| 372.33            | 3.4           | 464.53        | 3.66          |               |               | 338.6         | 3.1           | 417.00        | 3.27          | 240.73            | 8.02          | 633.73        | 8.62          | 300.8         | 39.72         | 241.87 | 10.11 |       |       |
| 372.93            | 6.31          | 537.87        | 11.89         |               |               | 408.73        | 3.06          | 456.93        | 13.74         | 248.6             | 8.91          | 634.07        | 13.97         | 316.73        | 20.73         | 242.6  | 12.3  |       |       |
| 373.2             | 6.17          | 538.87        | 6.99          |               |               | 456.93        | 11.39         | 457.93        | 3.02          | 285.8             | 7.53          | 731.07        | 9.8           | 316.93        | 22.03         | 242.87 | 12.69 |       |       |
| 374.2             | 3.04          | 568.8         | 4.33          |               |               | 472.93        | 30.42         | 472.93        | 25.84         | 300.07            | 15.49         |               |               | 364.8         | 10.39         | 248.73 | 37.61 |       |       |
| 408.4             | 3.38          |               |               |               |               | 474           | 5.32          | 473.93        | 4.77          | 300.6             | 89.88         |               |               | 365.07        | 10.9          | 267    | 69.81 |       |       |
| 435.6             | 24.58         |               |               |               |               | 504.67        | 3.61          | 510.93        | 3.15          | 301.67            | 12.01         |               |               | 380.8         | 18.95         | 273.87 | 6.56  |       |       |
| 455.67            | 7.67          |               |               |               |               | 526.8         | 3.03          | 526.87        | 3.34          | 301.87            | 6.77          |               |               | 407           | 9.92          | 300.47 | 14.57 |       |       |
| 472.67            | 4.69          |               |               |               |               | 536.93        | 11.5          | 536.87        | 7.96          | 317.4             | 6.31          |               |               | 471.13        | 31.11         | 300.87 | 27.09 |       |       |
| 472.87            | 4.81          |               |               |               |               | 537.87        | 5.27          | 537.87        | 3.78          | 364.67            | 10.48         |               |               | 471.87        | 8.35          | 301.87 | 6.87  |       |       |
| 537.47            | 6.42          |               |               |               |               | 568.8         | 20.47         | 568.87        | 12.47         | 365.33            | 6.13          |               |               | 472.33        | 6.23          | 316.4  | 9.64  |       |       |
|                   |               |               |               |               |               | 569.6         | 3.37          | 569.73        | 3.29          | 365.73            | 17.58         |               |               | 534.93        | 42.46         | 316.8  | 22.01 |       |       |
|                   |               |               |               |               |               | 569.87        | 4.29          | 741.07        | 5.58          | 396.6             | 7.1           |               |               | 536.07        | 6.74          | 364.73 | 15.48 |       |       |
|                   |               |               |               |               |               | 741.13        | 9.57          |               |               | 463.33            | 13.15         |               |               | 566.87        | 7.59          | 365    | 13.76 |       |       |
|                   |               |               |               |               |               | 742           | 3.48          |               |               | 470.67            | 9.97          |               |               | 568.93        | 19.81         | 380.4  | 7.74  |       |       |
|                   |               |               |               |               |               | 836.8         | 4.49          |               |               | 471.33            | 7.12          |               |               | 582.87        | 7.69          | 381    | 17.51 |       |       |
|                   |               |               |               |               |               | 837.07        | 4.06          |               |               | 503.73            | 8.32          |               |               | 584.87        | 6.08          | 381.93 | 9.72  |       |       |
|                   |               |               |               |               |               | 868.6         | 3.03          |               |               | 504.6             | 7.54          |               |               | 633.07        | 51.52         | 384.87 | 6.49  |       |       |
|                   |               |               |               |               |               | 868.87        | 3.06          |               |               | 541.6             | 6.25          |               |               | 634.2         | 8.81          | 407    | 11.59 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 552.93            | 6.62          |               |               | 648.73        | 6.5           | 446.8  | 8.73  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 568.67            | 42.04         |               |               | 730.8         | 16.01         | 471.07 | 44.53 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 569.6             | 44.73         |               |               | 739           | 10.42         | 473.07 | 6.51  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 569.8             | 47.08         |               |               | 739.27        | 15.97         | 479.07 | 6.07  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 570.33            | 6.93          |               |               | 739.8         | 6.31          | 484.8  | 6.65  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 570.53            | 7.21          |               |               | 803.33        | 14.19         | 504    | 6.89  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 605.8             | 6.52          |               |               | 804.27        | 6.62          | 535    | 41.7  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 632.33            | 8.55          |               |               | 836.8         | 9.09          | 536.13 | 11.94 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 632.6             | 9.52          |               |               | 837.13        | 15.22         | 560.87 | 7.87  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 632.87            | 11.98         |               |               | 859.27        | 8.22          | 566.73 | 6.28  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 665.67            | 6.48          |               |               | 875.2         | 7.59          | 567.07 | 10.24 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 704.67            | 6.62          |               |               |               |               | 568.53 | 8.78  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 732.07            | 6.51          |               |               |               |               | 568.87 | 19.69 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 733.13            | 7.33          |               |               |               |               | 569.6  | 9.07  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 786.13            | 6.5           |               |               |               |               | 585.13 | 10.35 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 836.47            | 10.56         |               |               |               |               | 598.73 | 7.4   |       |       |
|                   |               |               |               |               |               |               |               |               |               | 836.93            | 7.38          |               |               |               |               | 598.93 | 7.58  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 837.47            | 14.2          |               |               |               |               | 607    | 7.39  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 837.67            | 16.23         |               |               |               |               | 607.27 | 10.07 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 838               | 20.04         |               |               |               |               | 632.87 | 25.36 |       |       |
|                   |               |               |               |               |               |               |               |               |               | 838.8             | 19.68         |               |               |               |               | 634    | 9.4   |       |       |
|                   |               |               |               |               |               |               |               |               |               | 839.6             | 8.04          |               |               |               |               | 635    | 6.33  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 841.67            | 6.63          |               |               |               |               | 666.47 | 8.19  |       |       |
|                   |               |               |               |               |               |               |               |               |               | 887.33            | 6.85          |               |               |               |               | 667    | 6.08  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 671    | 6.44  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 697.33 | 6.08  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 704.93 | 8.72  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 730.93 | 11.61 |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 731.2  | 7.38  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 732.07 | 7.01  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 738.87 | 21.39 |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 739.27 | 6.89  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 739.53 | 6.17  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 768.87 | 6.28  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 772.07 | 7.63  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 803    | 8.48  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 803.27 | 9     |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 836.53 | 11.72 |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 837.13 | 12.25 |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 838    | 7.54  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 869.13 | 6.43  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 875.13 | 6.81  |       |       |
|                   |               |               |               |               |               |               |               |               |               |                   |               |               |               |               |               | 875.47 | 8.92  |       |       |

A low abundance signal in the positive ion ESI-MS from the solution at pH 5 ( $m/z_{\text{obs}}$  286.5, 3%) and pH 7 ( $m/z_{\text{obs}}$  286.4, 3%) was ascribed to the  $[M + H]^+$  adduct of  $[V^{\text{VO}}(\text{OH})(\text{sbhaH}_2)]$  ( $m/z_{\text{calc}}$  287.2) (Scheme S1, A), a structural analog of  $[V^{\text{VO}}(\text{OH})(\text{pb})]$  (5). A different type of coordination complex was attributed to signals from the solution at pH 7 in the positive ion ESI-MS ( $m/z_{\text{obs}}$  472.9, 30%) and in the negative ion ESI-MS ( $m/z_{\text{obs}}$  471.1, 31%). In these complexes,  $[V^{\text{VO}}(\text{sbhaH}_3)_2]^+$  ( $m/z_{\text{calc}}$  473.4) and  $[V^{\text{VO}}(\text{sbhaH}_2)_2]^-$  ( $m/z_{\text{calc}}$  471.4), the V center is bound by one coordinating hydroxamic acid group of sbhaH<sub>4</sub> with the second hydroxamic acid group of the same ligand non-coordinating (Scheme S1, B, C, D).

**Scheme S1**



|  |  |     |      |
|--|--|-----|------|
|  |  | 877 | 6.65 |
|--|--|-----|------|