Supporting Information

Chelate Coordination Compounds as a New Class of High-Energy Materials. The Case of Nitro-Bis(Acetylacetonato) Complexes.

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I Crystal structures extracted from Cambridge Structural Database

Figure S1. Crystal structures extracted from Cambridge Structural Database: LIYLIO (bis (acetylacetonato) cobalt (II)), FEVMUP (bis (acetylacetonato) nickel (II)), ACACC001 (bis (acetylacetonato) copper (II)), ASOCOC (bis (acetylacetonato) zinc (II)) and ACACVO07 (bis (acetylacetonato) oxovanadium (IV)).
II Cartesian coordinates for optimized geometries of chelate complexes

Table S1. Cartesian coordinates for optimized geometry of Co(acac)₂ complex

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | -1.27895 | 1.35443 | 0.00023 |
| O    | -1.27895 | -1.35443 | 0.00018 |
| C    | -2.54669 | 1.22412 | -0.00006 |
| C    | -3.22381 | 0.00000 | -0.00021 |
| C    | -2.54669 | -1.22412 | -0.00003 |
| C    | -3.31200 | 2.50991 | -0.00019 |
| C    | -3.31200 | -2.50991 | 0.00005 |
| H    | -4.31461 | 0.00000 | -0.00040 |
| H    | -3.02572 | 3.10294 | -0.88267 |
| H    | -3.02575 | 3.10311 | 0.88218 |
| H    | -4.39885 | 2.35632 | -0.00021 |
| H    | -4.39886 | -2.35632 | -0.00058 |
| H    | -3.02525 | -3.10338 | -0.88197 |
| H    | -3.02623 | -3.10266 | 0.88288 |
| H    | 3.02559 | -3.10313 | 0.88227 |
| H    | 3.02578 | 3.10297 | 0.88251 |
| C    | 3.31200 | -2.50991 | -0.00003 |
| H    | 4.39885 | -2.35632 | 0.00016 |
| C    | 2.54669 | -1.22412 | 0.00001 |
| C    | 3.22381 | 0.00000 | 0.00008 |
| H    | 4.31461 | 0.00000 | 0.00015 |
| O    | 1.27895 | -1.35443 | -0.00012 |
| C    | 2.54669 | 1.22412 | 0.00000 |
| C    | 3.31200 | 2.50991 | 0.00004 |
| O    | 1.27895 | 1.35443 | -0.00012 |
| H    | 4.39886 | 2.35632 | -0.00001 |
| H    | 3.02588 | -3.10292 | -0.88257 |
| H    | 3.02570 | 3.10308 | -0.88233 |
| Co   | 0.00000 | 0.00000 | 0.00005 |
Table S2. Cartesian coordinates for optimized geometry of Co(acac-NO$_2$)$_2$ complex

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | -1.29948 | 1.34032 | 0.07189 |
| O    | -1.29310 | -1.33806 | -0.06695 |
| C    | -2.55875 | 1.25164 | 0.05448 |
| C    | -3.23500 | -0.00255 | 0.00191 |
| C    | -2.56224 | -1.24664 | -0.04875 |
| C    | -3.27245 | 2.56241 | 0.13702 |
| C    | -3.26669 | -2.56198 | -0.12468 |
| N    | -4.69257 | -0.00219 | -0.00214 |
| H    | -3.64077 | 2.84411 | -0.86033 |
| H    | -2.55508 | 3.31424 | 0.48768 |
| H    | -4.15368 | 2.52532 | 0.79008 |
| H    | -4.15996 | -2.53257 | -0.76106 |
| H    | -2.54847 | -3.30725 | -0.48753 |
| H    | -3.61378 | -2.84917 | 0.87906 |
| H    | 3.63974 | -2.84510 | 0.85812 |
| H    | 2.54843 | 3.30680 | 0.49030 |
| C    | 3.27234 | -2.56238 | -0.13925 |
| H    | 4.15419 | -2.52472 | -0.79149 |
| C    | 2.55867 | -1.25159 | -0.05627 |
| C    | 3.23495 | 0.00248 | -0.00114 |
| N    | 4.69255 | 0.00200 | 0.00509 |
| O    | 1.29940 | -1.34015 | -0.07591 |
| C    | 2.56230 | 1.24661 | 0.04946 |
| C    | 3.26691 | 2.56175 | 0.12751 |
| O    | 1.29313 | 1.33830 | 0.06569 |
| H    | 4.15947 | 2.53158 | 0.76485 |
| H    | 2.55530 | -3.31377 | -0.49152 |
| H    | 3.61514 | 2.84988 | -0.87557 |
| Co   | 0.00000 | 0.00013 | -0.00161 |
| O    | 5.26023 | -0.89511 | 0.60554 |
| O    | 5.26871 | 0.89765 | -0.5893 |
| O    | -5.26123 | 0.89438 | -0.60255 |
| O    | -5.26777 | -0.89735 | 0.59389 |
Table S3. Cartesian coordinates for optimized geometry of Ni(acac)$_2$ complex

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | 1.25847 | -1.36345 | 0.00045 |
| O    | 1.25850 | 1.36343  | 0.00030 |
| C    | 2.52234 | -1.22463 | -0.00005 |
| C    | 3.20021 | -0.00002 | -0.00039 |
| C    | 2.52235 | 1.22463  | -0.00001 |
| C    | 3.29319 | -2.50871 | -0.00021 |
| C    | 3.29326 | 2.50868  | 0.00018  |
| H    | 4.29114 | 0.00000  | -0.00068 |
| H    | 3.00849 | -3.10229 | -0.88292 |
| H    | 3.00874 | -3.10235 | 0.88255  |
| H    | 4.37954 | -2.35029 | -0.00038 |
| H    | 4.37959 | 2.35020  | -0.00086 |
| H    | 3.00790 | 3.10302  | -0.88179 |
| H    | 3.00954 | 3.10159  | 0.88367  |
| H    | -3.00835 | 3.10254  | 0.88234  |
| H    | -3.00879 | -3.10222 | 0.88293  |
| C    | -3.29321 | 2.50871  | -0.00015 |
| H    | -4.37956 | 2.35028  | 0.00023  |
| C    | -2.52235 | 1.22463  | -0.00011 |
| C    | -3.20021 | 0.00002  | 0.00012  |
| H    | -4.29115 | -0.00002 | 0.00026  |
| O    | -1.25847 | 1.36345  | -0.00028 |
| C    | -2.52235 | -1.22463 | 0.00003  |
| C    | -3.29324 | -2.50868 | 0.00011  |
| O    | -1.25849 | -1.36343 | -0.00013 |
| H    | -4.37958 | -2.35021 | -0.00004 |
| H    | -3.00895 | 3.10210  | -0.88314 |
| H    | -3.00859 | 3.10241  | -0.88252 |
| Ni   | 0.00000 | 0.00000  | 0.00002  |
Table S4. Cartesian coordinates for optimized geometry of Ni(acac-NO₂)₂ complex

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | 1.26654 | 1.33480 | 0.07266 |
| O    | 1.26650 | -1.33483 | -0.07279 |
| C    | 2.52887 | 1.24670 | 0.05095 |
| C    | 3.20803 | 0.00005 | 0.00000 |
| C    | 2.52883 | -1.24680 | -0.05104 |
| C    | 3.23084 | 2.56418 | 0.12684 |
| C    | 3.23068 | -2.56434 | -0.12705 |
| H    | 2.50668 | 3.31264 | 0.47051 |
| H    | 3.60066 | 2.84109 | -0.87120 |
| H    | 4.11048 | 2.53684 | 0.78240 |
| H    | 3.60049 | -2.84137 | 0.87096 |
| H    | 2.50641 | -3.31270 | -0.47074 |
| H    | 4.11028 | -2.53708 | -0.78266 |
| H    | -2.50686 | -3.31266 | -0.47053 |
| H    | -3.60047 | 2.84125 | -0.87115 |
| H    | -4.11066 | -2.53674 | -0.78219 |
| C    | -3.23092 | -2.56414 | -0.12675 |
| N    | -4.66362 | -0.00002 | -0.00007 |
| C    | -3.20799 | 0.00004 | 0.00000 |
| C    | -2.52887 | -1.24671 | -0.05099 |
| C    | -3.23078 | 2.56427 | 0.12692 |
| C    | -2.52883 | 1.24678 | 0.05106 |
| O    | -1.26654 | -1.33481 | -0.07269 |
| H    | -4.11049 | 2.53694 | 0.78238 |
| O    | -1.26650 | 1.33484 | 0.07279 |
| H    | -3.60062 | -2.84102 | 0.87135 |
| H    | -2.50663 | 3.31271 | 0.47071 |
| Ni   | 0.00000 | 0.00000 | -0.00001 |
| N    | 4.66367 | 0.00002 | 0.00009 |
| O    | 5.23656 | 0.91211 | -0.5728 |
| O    | 5.23663 | -0.91201 | 0.57298 |
| O    | -5.23649 | -0.91233 | 0.57247 |
| O    | -5.23655 | 0.91231 | -0.57254 |
Table S5. Cartesian coordinates for optimized geometry of Cu(acac)$_2$ complex

| atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| O    | -1.33117  | -1.39535  | 0.00012   |
| O    | -1.33117  | 1.39535   | -0.00013  |
| C    | -2.59111  | -1.23407  | 0.00011   |
| C    | -3.25717  | 0.00000   | 0.00001   |
| C    | -2.59111  | 1.23407   | -0.00011  |
| C    | -3.38994  | -2.50336  | 0.00021   |
| C    | -3.38994  | 2.50336   | -0.00036  |
| H    | -3.11455  | -3.10228  | 0.88243   |
| H    | -3.11476  | -3.10222  | -0.88211  |
| H    | -4.47378  | -2.32750  | 0.00032   |
| H    | -3.11439  | 3.10257   | 0.88161   |
| H    | -3.11492  | 3.10193   | -0.88293  |
| H    | -4.47378  | 2.32750   | 0.00000   |
| H    | 3.11495   | 3.10214   | -0.88223  |
| H    | 3.11459   | -3.10207  | -0.88274  |
| H    | 4.47378   | 2.32750   | 0.00056   |
| C    | 3.38994   | 2.50336   | 0.00020   |
| C    | 3.25717   | 0.00000   | -0.00006  |
| C    | 2.59111   | 1.23407   | 0.00009   |
| C    | 3.38994   | -2.50336  | -0.00037  |
| C    | 2.59111   | -1.23407  | -0.00008  |
| O    | 1.33117   | 1.39535   | 0.00026   |
| H    | 4.47378   | -2.32750  | -0.00044  |
| O    | 1.33117   | -1.39535  | -0.00002  |
| H    | 3.11436   | 3.10236   | 0.88230   |
| H    | 3.11472   | -3.10242  | 0.88179   |
| Cu   | 0.00000   | -0.00000  | 0.00007   |
| H    | 4.34848   | 0.00000   | -0.00015  |
| H    | -4.34848  | 0.00000   | 0.00001   |
### Table S6. Cartesian coordinates for optimized geometry of Cu(acac-NO$_2$)$_2$ complex

| atom | x       | y       | z       |
|------|---------|---------|---------|
| O    | -1.34631| -1.36085| 0.06962 |
| O    | -1.34632| 1.36084 | -0.06928|
| C    | -2.60569| -1.25496| 0.05229 |
| C    | -3.27452| -0.00001| 0.00004 |
| C    | -2.60569| 1.25494 | -0.05210|
| C    | -3.33384| -2.56012| 0.13508 |
| C    | -3.33385| 2.56010 | -0.13487|
| H    | -2.62471| -3.31642| 0.49312 |
| H    | -3.69508| -2.84205| -0.86483|
| H    | -4.21981| -2.51544| 0.78117 |
| H    | -3.69521| 2.84196 | 0.86502 |
| H    | -2.62471| 3.31643 | -0.49280|
| H    | -4.21977| 2.51543 | -0.78104|
| H    | 2.62437 | 3.31645 | -0.49261|
| H    | 3.69529 | -2.84202| -0.86508|
| H    | 4.21947 | 2.51572 | -0.78124|
| C    | 3.33370 | 2.56020 | -0.13488|
| N    | 4.73223 | -0.00001| 0.00006 |
| C    | 3.27457 | -0.00001| -0.00002|
| C    | 2.60569 | 1.25496 | -0.05201|
| C    | 3.33370 | -2.56021| 0.13474 |
| C    | 2.60570 | -1.25498| 0.05187 |
| O    | 1.34632 | 1.36082 | -0.06937 |
| H    | 4.21943 | -2.51576| 0.78118 |
| O    | 1.34632 | 1.36085 | 0.06913 |
| H    | 3.69520 | 2.84205 | 0.86496 |
| H    | 2.62436 | -3.31650| 0.49238 |
| Cu   | 0.00000 | -0.00001| 0.00002 |
| N    | -4.73216| -0.00002| -0.00007|
| O    | -5.30501| -0.88265| -0.61738|
| O    | -5.30511| 0.88273 | 0.617  |
| O    | 5.30514 | 0.88203 | 0.61821 |
| O    | 5.30523 | -0.88193| -0.61813|
Table S7. Cartesian coordinates for optimized geometry of Zn(acac)$_2$ complex

| atom | x      | y      | z      |
|------|--------|--------|--------|
| H    | -4.06654 | 2.37792 | -1.13680 |
| C    | -3.41054 | 1.74784 | -1.75790 |
| H    | -2.79019 | 2.38621 | -2.39878 |
| H    | -4.07322 | -1.11781 | 2.38002 |
| C    | -2.53967 | 0.88480 | -0.89052 |
| C    | -3.17380 | 0.00266 | -0.00015 |
| H    | -4.26757 | 0.00517 | 0.00052 |
| O    | -1.28443 | 1.02943 | -1.03988 |
| C    | -2.54264 | -0.88304 | 0.88877 |
| C    | -3.41636 | -1.74373 | 1.75565 |
| H    | -4.06526 | 1.12321 | -2.38586 |
| O    | -1.28789 | -1.03356 | 1.03664 |
| H    | -2.79805 | -2.38089 | 2.39970 |
| H    | -4.07022 | -2.37531 | 1.13377 |
| H    | 4.06891  | -2.38378 | -1.11791 |
| C    | 3.41630  | -1.75519 | -1.74414 |
| H    | 2.79799  | -2.39557 | -2.38497 |
| H    | 4.06393  | 1.13796  | 2.37990 |
| C    | 2.54264  | -0.88871 | -0.88302 |
| C    | 3.17380  | 0.00258  | 0.00025 |
| H    | 4.26758  | 0.00470  | -0.00011 |
| O    | 1.28786  | -1.03981 | -1.03016 |
| C    | 2.53967  | 0.89074  | 0.88467 |
| C    | 3.41059  | 1.75892  | 1.74688 |
| H    | 4.07441  | -1.13361 | -2.37151 |
| O    | 1.28446  | 1.03692  | 1.03261 |
| H    | 2.79025  | 2.40235  | 2.38269 |
| H    | 4.06796  | 2.38392  | 1.12213 |
| Zn   | 0.00000  | -0.00265 | 0.00002 |
Table S8. Cartesian coordinates for optimized geometry of Zn(acac-NO₂)₂ complex

| atom | x    | y    | z     |
|------|------|------|-------|
| H    | -4.24193 | 2.30994 | -1.19750 |
| C    | -3.35018 | 1.91182 | -1.69825 |
| H    | -2.66544 | 2.72240 | -1.97666 |
| H    | -3.70448 | -1.40818 | 2.60986 |
| C    | -2.58374 | 0.93937 | -0.85710 |
| C    | -3.22783 | -0.00008 | 0.00010 |
| N    | -4.69062 | -0.00044 | 0.00015 |
| O    | -1.32545 | 1.04863 | -0.94780 |
| C    | -2.58325 | -0.93923 | 0.85727 |
| C    | -3.34919 | -1.91193 | 1.69860 |
| H    | -3.70543 | 1.40798 | -2.60948 |
| O    | -1.32491 | -1.04796 | 0.94784 |
| H    | -2.66409 | -2.72223 | 1.97694 |
| H    | -4.24089 | -2.31040 | 1.19803 |
| H    | 3.70367 | -2.61074 | -1.40733 |
| C    | 3.34948 | -1.69917 | -1.91129 |
| H    | 2.66478 | -1.97699 | -2.72212 |
| H    | 4.24093 | 1.19772 | 2.31075 |
| C    | 2.58340 | -0.85738 | -0.93911 |
| C    | 3.22786 | -0.00010 | 0.00003 |
| N    | 4.69062 | -0.00034 | -0.00006 |
| O    | 1.32509 | -0.94768 | -1.04829 |
| C    | 2.58362 | 0.85755 | 0.93897 |
| C    | 3.34985 | 1.69878 | 1.91154 |
| H    | 4.24186 | -1.19928 | -2.30904 |
| O    | 1.32531 | 0.94861 | 1.04769 |
| H    | 2.66461 | 1.97810 | 2.72139 |
| H    | 3.70606 | 2.60950 | 1.40746 |
| Zn   | 0.00001 | 0.00051 | -0.00019 |
| O    | 5.2626 | 1.07092 | 0.11081 |
| O    | 5.26214 | -1.07187 | -0.11077 |
| O    | -5.26233 | -0.11186 | 1.0715 |
| O    | -5.26246 | 0.11051 | -1.07119 |
Table S9. Cartesian coordinates for optimized geometry of VO(acac)$_2$ complex

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | 1.32541 | 1.35648 | -0.08666 |
| O    | 1.32597 | -1.35643 | -0.08618 |
| C    | 3.25893 | 0.00040 | -0.27239 |
| C    | 2.58464 | 1.22712 | -0.23744 |
| C    | 2.58521 | -1.22663 | -0.23682 |
| C    | 3.33940 | 2.50520 | -0.41283 |
| C    | 3.34050 | -2.50447 | -0.41157 |
| H    | 3.16143 | 3.14828 | 0.46284 |
| H    | 4.41796 | 2.35029 | -0.54383 |
| H    | 2.93493 | 3.04405 | -1.28367 |
| H    | 3.16125 | -3.14806 | 0.46343 |
| H    | 2.93759 | -3.04292 | -1.28340 |
| H    | 4.41921 | -2.34925 | -0.54095 |
| H    | -4.41906 | 2.34941 | -0.54002 |
| C    | -3.34020 | 2.50459 | -0.41183 |
| H    | -3.15997 | 3.14894 | 0.46241 |
| C    | -2.58488 | 1.22678 | -0.23680 |
| C    | -3.25875 | -0.00021 | -0.27160 |
| O    | -1.32561 | 1.35659 | -0.08669 |
| H    | -3.15849 | -3.14966 | 0.46090 |
| H    | -2.93811 | 3.04221 | -1.28456 |
| C    | -2.58457 | -1.22699 | -0.23769 |
| O    | -1.32511 | -1.35649 | -0.08845 |
| C    | -3.33955 | -2.50495 | -0.41292 |
| H    | -2.93783 | -3.04202 | -1.28615 |
| H    | -4.41855 | -2.35009 | -0.54024 |
| V    | -0.00009 | -0.00017 | 0.49699 |
| H    | -4.34021 | -0.00030 | -0.41310 |
| H    | 4.34027 | 0.00062 | -0.41475 |
| O    | -0.00099 | -0.0005 | 2.06071 |
Table S10. Cartesian coordinates for optimized geometry of VO(acac-NO$_2$)$_2$ complex

| atom | x   | y   | z    |
|------|-----|-----|------|
| O    | 1.34218 | 1.32359 | -0.06589 |
| O    | 1.34058 | -1.32611 | 0.08122 |
| C    | 3.27582 | -0.01505 | -0.15423 |
| C    | 2.60006 | 1.23395 | -0.20124 |
| C    | 2.59752 | -1.26112 | -0.07800 |
| C    | 3.28987 | 2.52876 | -0.47723 |
| C    | 3.28693 | -2.58166 | -0.16731 |
| H    | 3.68120 | 2.92957 | 0.47061 |
| H    | 4.14743 | 2.43291 | -1.15378 |
| H    | 2.54412 | 3.22833 | -0.87499 |
| H    | 2.58304 | -3.35397 | 0.16457 |
| H    | 3.59358 | -2.77342 | -1.20587 |
| H    | 4.20869 | -2.60826 | 0.42876 |
| H    | -4.14702 | 2.43343 | -1.15279 |
| C    | -3.29001 | 2.52905 | -0.47552 |
| H    | -3.68201 | 2.92966 | 0.47213 |
| C    | -2.60048 | 1.23412 | -0.19929 |
| C    | -3.27632 | -0.01481 | -0.15337 |
| O    | -1.34276 | 1.32373 | -0.06253 |
| H    | -2.58505 | -3.35330 | 0.17165 |
| H    | -2.54394 | 3.22871 | -0.87251 |
| C    | -2.59840 | -1.26090 | -0.07463 |
| O    | -1.34173 | -1.32602 | 0.08641 |
| C    | -3.28801 | -2.58139 | -0.16311 |
| H    | -3.59175 | -2.77478 | -1.20227 |
| H    | -4.21134 | -2.60701 | 0.43049 |
| V    | 0.00050 | 0.03243 | 0.60326 |
| N    | -4.72907 | -0.00864 | -0.27977 |
| O    | 0.00364 | 0.11783 | 2.15880 |
| O    | -5.3358 | 0.90173 | 0.25774 |
| O    | -5.25931 | -0.90857 | -0.90862 |
| N    | 4.72868 | -0.00869 | -0.27796 |
| O    | 5.33419 | 0.9022 | 0.26015 |
| O    | 5.26057 | -0.90866 | -0.90518 |
III Vibrational frequencies

Figure S2. Calculated infrared spectrum for optimized geometry of Co(acac)\textsubscript{2} complex

Figure S3. Calculated infrared spectrum for optimized geometry of Co(acac-NO\textsubscript{2})\textsubscript{2} complex
Figure S4. Calculated infrared spectrum for optimized geometry of Ni(acac)$_2$ complex

Figure S5. Calculated infrared spectrum for optimized geometry of Ni(acac-NO$_2$)$_2$ complex
Figure S6. Calculated infrared spectrum for optimized geometry of Cu(acac)$_2$ complex

Figure S7. Calculated infrared spectrum for optimized geometry of Cu(acac-NO$_2$)$_2$ complex
Figure S8. Calculated infrared spectrum for optimized geometry of Zn(acac)$_2$ complex

Figure S9. Calculated infrared spectrum for optimized geometry of Zn(acac-NO$_2$)$_2$ complex
Figure S10. Calculated infrared spectrum for optimized geometry of VO(acac)$_2$ complex

Figure S11. Calculated infrared spectrum for optimized geometry of VO(acac-NO$_2$)$_2$ complex
**IV Bond dissociation energies (without zero-potential energy correction)**

**Table S11.** Calculated bond dissociation energies (without zero-potential energy correction) of weakest C-NO₂ bonds in studied nitro-bis(acetylacetonato) complexes.

| Complex          | E (complex)¹   | E (complex radical)¹ | E (NO₂ radical)¹ | BDE²   |
|------------------|----------------|----------------------|------------------|--------|
| Co(acac-NO₂)₂    | -2482.316510   | -2277.092658         | -205.128032      | 60.13  |
| Ni(acac-NO₂)₂    | -2607.862277   | -2402.636087         | -205.128032      | 61.60  |
| Cu(acac-NO₂)₂    | -2740.033947   | -2534.809344         | -205.128032      | 60.60  |
| Zn(acac-NO₂)₂    | -2878.904750   | -2673.682471         | -205.128032      | 59.14  |
| VO(acacNO₂)₂     | -2118.900795   | -1913.646821         | -205.128032      | 78.03  |

¹ Energies given in Hartrees  
² Energies given in kcal/mol

**V Calculated electrostatic potential maps for the modified structures of (bis (acetylacetonato) and nitro-bis (acetylacetonato) oxovanadium (IV) complexes**

**Figure S12.** Calculated electrostatic potential maps of modified bis (acetylacetonato) and nitro-bis (acetylacetonato) oxovanadium (IV) complexes (-CH₃ groups substituted with H atoms).