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**Supporting information for article:**

# Structure-directing sulfur···metal noncovalent semicoordination bonding

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**Table S1.** The equilibrium nuclei coordinates of the EGAXAN isolated molecule.

| | | | |
|---|---|---|---|
| I1 | 2.84035 | -0.00004 | 0.16947 |
| Ni2 | 0.32125 | 0.00006 | -0.21843 |
| P3 | 0.24770 | -2.20637 | -0.17183 |
| S4 | -1.93096 | -0.00041 | 1.92156 |
| P5 | 0.24773 | 2.20645 | -0.17138 |
| C6 | -1.88354 | 0.00049 | -2.06089 |
| H7 | -1.12093 | 0.00069 | -2.83689 |
| C8 | -1.49589 | 0.00021 | -0.71976 |
| C9 | -2.51489 | -0.00001 | 0.24685 |
| C10 | -3.86119 | -0.00001 | -0.11199 |
| H11 | -4.64095 | -0.00024 | 0.64164 |
| C12 | -3.22741 | 0.00053 | -2.43492 |
| H13 | -3.49922 | 0.00074 | -3.48610 |
| C14 | 0.91847 | 2.95050 | 1.35531 |
| H15 | 0.87611 | 4.04227 | 1.30339 |
| H16 | 1.94823 | 2.61762 | 1.49138 |
| H17 | 0.32199 | 2.60039 | 2.20067 |
| C18 | -1.37209 | -3.04136 | -0.31869 |
| H19 | -1.23961 | -4.12649 | -0.28989 |
| H20 | -1.85870 | -2.75165 | -1.25153 |
| H21 | -2.01212 | -2.72909 | 0.50854 |
| C22 | 1.21100 | 2.98506 | -1.51456 |
| H23 | 0.79196 | 2.68223 | -2.47709 |
| H24 | 2.24230 | 2.63321 | -1.45603 |
| H25 | 1.17919 | 4.07538 | -1.43464 |
| C26 | -1.37219 | 3.04135 | -0.31747 |
| H27 | -1.23986 | 4.12648 | -0.28807 |
| H28 | -2.01209 | 2.72849 | 0.50962 |
| H29 | -1.85883 | 2.75213 | -1.25045 |
| C30 | -4.21485 | 0.00025 | -1.45866 |
| H31 | -5.26358 | 0.00026 | -1.73730 |
| C32 | 0.91777 | -2.95052 | 1.35510 |
| H33 | 0.32132 | -2.60003 | 2.20032 |
| H34 | 1.94767 | -2.61809 | 1.49131 |
| H35 | 0.87494 | -4.04227 | 1.30331 |
| C36 | 1.21167 | -2.98489 | -1.51457 |
| H37 | 2.24294 | -2.63305 | -1.45549 |
| H38 | 0.79314 | -2.68197 | -2.47730 |
| H39 | 1.17979 | -4.07521 | -1.43476 |
| C40 | -3.45177 | -0.00061 | 2.89573 |
| H41 | -4.04753 | 0.89479 | 2.70660 |
| H42 | -3.13831 | -0.00105 | 3.94080 |
| H43 | -4.04781 | -0.89568 | 2.70592 |

**Table S2.** The equilibrium nuclei coordinates of the PAJDIP isolated molecule.

| | | | |
|---|---|---|---|
| C1 | -1.21770 | 1.81062 | -1.29042 |
| C2 | -3.09555 | 2.89079 | -2.27022 |
| H3 | -3.44041 | 2.20947 | -3.05703 |
| H4 | -3.38539 | 3.90841 | -2.53533 |
| C5 | -3.67312 | 2.48302 | -0.92856 |
| H6 | -4.68144 | 2.08445 | -1.01269 |
| H7 | -3.66289 | 3.30960 | -0.21812 |
| C8 | 1.02173 | 1.23461 | 1.27968 |
| C9 | 2.03264 | 2.19253 | 1.24154 |
| H10 | 2.59960 | 2.34379 | 0.33064 |
| C11 | 2.31876 | 2.94150 | 2.36965 |
| H12 | 3.10835 | 3.68237 | 2.33924 |
| C13 | 1.59934 | 2.73809 | 3.54085 |
| H14 | 1.82848 | 3.32231 | 4.42384 |
| C15 | 0.59453 | 1.78432 | 3.58284 |
| H16 | 0.03631 | 1.62041 | 4.49626 |
| C17 | 0.30500 | 1.03176 | 2.45382 |
| H18 | -0.47483 | 0.27907 | 2.47900 |
| C19 | 2.19489 | -0.13206 | -0.94302 |
| C20 | 2.90859 | -1.19204 | -0.38976 |
| H21 | 2.47917 | -1.76293 | 0.42626 |
| C22 | 4.15601 | -1.52332 | -0.88970 |
| H23 | 4.70697 | -2.34966 | -0.45815 |
| C24 | 4.69226 | -0.80504 | -1.95045 |
| H25 | 5.66535 | -1.06968 | -2.34586 |
| C26 | 3.97795 | 0.24360 | -2.50930 |
| H27 | 4.39210 | 0.79924 | -3.34190 |
| C28 | 2.72976 | 0.58353 | -2.00750 |
| H29 | 2.15853 | 1.39573 | -2.43745 |
| N30 | 0.00498 | 1.43850 | -1.28669 |
| N31 | -1.66416 | 2.80866 | -2.09286 |
| Au32 | -0.70608 | -1.48378 | 0.21292 |
| Cl33 | -2.00262 | -3.30288 | 0.65948 |
| P34 | 0.59148 | 0.28788 | -0.21321 |
| S35 | -2.56254 | 1.17170 | -0.32401 |
| H36 | -1.03321 | 3.10781 | -2.81831 |

**Table S3.** The equilibrium nuclei coordinates of the PAJDOV isolated molecule.

| | | | |
|---|---|---|---|
| Au1 | -0.79244 | -1.45277 | 0.19937 |
| P2 | 0.58429 | 0.25445 | -0.24024 |
| Cl3 | -2.18230 | -3.19608 | 0.65503 |
| N4 | 0.07863 | 1.35360 | -1.39730 |
| N5 | -1.55347 | 2.69129 | -2.36121 |
| H6 | -0.91318 | 2.99790 | -3.07371 |
| C7 | -1.12144 | 1.80681 | -1.41917 |
| C8 | -2.86814 | 3.08631 | -2.27887 |
| H9 | -3.26188 | 3.77524 | -3.00938 |
| C10 | -3.52004 | 2.53452 | -1.24981 |
| H11 | -4.55030 | 2.67569 | -0.97212 |
| C12 | 2.21617 | -0.23321 | -0.85398 |
| C13 | 2.88776 | -1.25407 | -0.18644 |
| H14 | 2.41311 | -1.75499 | 0.65024 |
| C15 | 4.15265 | -1.63588 | -0.59852 |
| H16 | 4.67118 | -2.43162 | -0.07839 |
| C17 | 4.74867 | -1.00727 | -1.68406 |
| H18 | 5.73581 | -1.31143 | -2.01008 |
| C19 | 4.07636 | 0.00204 | -2.35592 |
| H20 | 4.53736 | 0.48733 | -3.20765 |
| C21 | 2.81026 | 0.39209 | -1.94323 |
| H22 | 2.27084 | 1.17350 | -2.46214 |
| C23 | 0.95307 | 1.25829 | 1.23386 |
| C24 | 0.21314 | 1.08291 | 2.39765 |
| H25 | -0.55223 | 0.31547 | 2.43206 |
| C26 | 0.46159 | 1.88008 | 3.50621 |
| H27 | -0.11569 | 1.73803 | 4.41138 |
| C28 | 1.44858 | 2.85116 | 3.45334 |
| H29 | 1.64525 | 3.47090 | 4.31977 |
| C30 | 2.19147 | 3.02806 | 2.29199 |
| H31 | 2.96720 | 3.78309 | 2.25379 |
| C32 | 1.94597 | 2.23507 | 1.18510 |
| H33 | 2.53026 | 2.36580 | 0.28180 |
| S34 | -2.48082 | 1.47033 | -0.34354 |

**Table S4.** The equilibrium nuclei coordinates of the WOVJOG01 isolated molecule.

| | | | |
|---|---|---|---|
| PT1 | 0.00001 | 0.00029 | 0.00000 |
| S1 | -2.90371 | 1.19199 | 0.02140 |
| N1 | -0.86183 | -0.04599 | -1.81665 |
| H1N | -0.33276 | -0.49881 | -2.54832 |
| N2 | -2.87089 | 1.23381 | -1.64294 |
| C1 | -1.92335 | 0.57244 | -2.29103 |
| C2 | -2.13561 | 0.58237 | -3.77990 |
| H2A | -1.49867 | -0.14324 | -4.28748 |
| H2B | -1.90456 | 1.57607 | -4.16991 |
| H2C | -3.17944 | 0.37676 | -4.01493 |
| C3 | -4.68367 | 1.20487 | 0.29079 |
| C4 | -5.56823 | 1.43556 | -0.74725 |
| H4 | -5.18907 | 1.58946 | -1.74917 |
| C5 | -6.92699 | 1.44925 | -0.46503 |
| H5 | -7.63693 | 1.63445 | -1.26277 |
| C6 | -7.37731 | 1.23190 | 0.83036 |
| H6 | -8.43985 | 1.24976 | 1.04292 |
| C7 | -6.47148 | 0.99555 | 1.85661 |
| H7 | -6.82429 | 0.82551 | 2.86691 |
| C8 | -5.11128 | 0.97501 | 1.58943 |
| H8 | -4.39767 | 0.78785 | 2.38481 |
| C9 | -2.52627 | 2.87750 | 0.51476 |
| C10 | -1.80046 | 3.05984 | 1.67966 |
| H10 | -1.43985 | 2.20414 | 2.23849 |
| C11 | -1.54838 | 4.35398 | 2.11589 |
| H11 | -0.98384 | 4.51679 | 3.02643 |
| C12 | -2.02658 | 5.43455 | 1.38964 |
| H12 | -1.83218 | 6.44359 | 1.73317 |
| C13 | -2.75551 | 5.23027 | 0.22342 |
| H13 | -3.13100 | 6.07864 | -0.33639 |
| C14 | -3.01341 | 3.94488 | -0.22347 |
| H14 | -3.57876 | 3.76659 | -1.13027 |
| S2 | -1.44212 | -2.80662 | -0.52626 |
| N3 | -0.62407 | -1.85240 | 0.52286 |
| H3N | -1.02051 | -1.91211 | 1.45657 |
| C15 | -1.32273 | -4.44356 | 0.21152 |
| C16 | -2.14523 | -5.45081 | -0.27744 |
| H16 | -2.89191 | -5.24372 | -1.03575 |
| C17 | -2.01226 | -6.72792 | 0.24136 |
| H17 | -2.65095 | -7.52307 | -0.12426 |
| C18 | -1.07014 | -6.98661 | 1.23074 |
| H18 | -0.97671 | -7.98654 | 1.63757 |
| C19 | -0.25228 | -5.96939 | 1.69722 |

| | | | |
|---|---|---|---|
| H19 | 0.48562 | -6.17276 | 2.46436 |
| C20 | -0.36448 | -4.68534 | 1.17952 |
| H20 | 0.29122 | -3.88866 | 1.50674 |
| C21 | -3.21477 | -2.53352 | -0.40187 |
| C22 | -3.88043 | -2.69915 | 0.80626 |
| H22 | -3.34616 | -3.02266 | 1.69338 |
| C23 | -5.24574 | -2.47708 | 0.85158 |
| H23 | -5.78223 | -2.60645 | 1.78390 |
| C24 | -5.93196 | -2.10945 | -0.30111 |
| H24 | -7.00153 | -1.94343 | -0.25919 |
| C25 | -5.25555 | -1.94866 | -1.50017 |
| H25 | -5.79453 | -1.66318 | -2.39545 |
| C26 | -3.88420 | -2.15886 | -1.55707 |
| H26 | -3.34430 | -2.04127 | -2.48967 |
| S1A | 2.90332 | -1.19216 | -0.02142 |
| N1A | 0.86189 | 0.04656 | 1.81664 |
| H1NA | 0.33300 | 0.49962 | 2.54829 |
| N2A | 2.87061 | -1.23377 | 1.64293 |
| C1A | 1.92329 | -0.57208 | 2.29101 |
| C2A | 2.13563 | -0.58189 | 3.77987 |
| H2AA | 1.49920 | 0.14422 | 4.28736 |
| H2BA | 1.90393 | -1.57538 | 4.17006 |
| H2CA | 3.17962 | -0.37695 | 4.01480 |
| C3A | 4.68326 | -1.20535 | -0.29094 |
| C4A | 5.56787 | -1.43593 | 0.74709 |
| H4A | 5.18876 | -1.58960 | 1.74906 |
| C5A | 6.92661 | -1.44985 | 0.46478 |
| H5A | 7.63659 | -1.63497 | 1.26251 |
| C6A | 7.37687 | -1.23281 | -0.83069 |
| H6A | 8.43939 | -1.25085 | -1.04332 |
| C7A | 6.47100 | -0.99657 | -1.85693 |
| H7A | 6.82375 | -0.82679 | -2.86729 |
| C8A | 5.11082 | -0.97581 | -1.58966 |
| H8A | 4.39718 | -0.78873 | -2.38502 |
| C9A | 2.52565 | -2.87769 | -0.51457 |
| C10A | 1.80004 | -3.06007 | -1.67959 |
| H10A | 1.43966 | -2.20441 | -2.23861 |
| C11A | 1.54785 | -4.35424 | -2.11569 |
| H11A | 0.98346 | -4.51709 | -3.02631 |
| C12A | 2.02573 | -5.43478 | -1.38919 |
| H12A | 1.83123 | -6.44384 | -1.73260 |
| C13A | 2.75447 | -5.23045 | -0.22285 |
| H13A | 3.12970 | -6.07879 | 0.33715 |
| C14A | 3.01249 | -3.94503 | 0.22389 |
| H14A | 3.57769 | -3.76669 | 1.13079 |

| | | | |
|---|---|---|---|
| S2A | 1.44251 | 2.80694 | 0.52631 |
| N3A | 0.62397 | 1.85303 | -0.52272 |
| H3NA | 1.01993 | 1.91305 | -1.45660 |
| C15A | 1.32350 | 4.44391 | -0.21147 |
| C16A | 2.14721 | 5.45070 | 0.27644 |
| H16A | 2.89467 | 5.24321 | 1.03386 |
| C17A | 2.01441 | 6.72785 | -0.24231 |
| H17A | 2.65403 | 7.52263 | 0.12248 |
| C18A | 1.07126 | 6.98706 | -1.23057 |
| H18A | 0.97797 | 7.98701 | -1.63737 |
| C19A | 0.25221 | 5.97030 | -1.69599 |
| H19A | -0.48650 | 6.17408 | -2.46225 |
| C20A | 0.36422 | 4.68623 | -1.17833 |
| H20A | -0.29233 | 3.88992 | -1.50475 |
| C21A | 3.21507 | 2.53330 | 0.40174 |
| C22A | 3.88060 | 2.69833 | -0.80653 |
| H22A | 3.34627 | 3.02156 | -1.69372 |
| C23A | 5.24586 | 2.47599 | -0.85195 |
| H23A | 5.78226 | 2.60489 | -1.78439 |
| C24A | 5.93216 | 2.10869 | 0.30080 |
| H24A | 7.00170 | 1.94246 | 0.25881 |
| C25A | 5.25588 | 1.94847 | 1.50001 |
| H25A | 5.79492 | 1.66323 | 2.39532 |
| C26A | 3.88458 | 2.15895 | 1.55700 |
| H26A | 3.34477 | 2.04180 | 2.48972 |

**Table S5.** The equilibrium nuclei coordinates of the isolated ionic pair from the CEWROM structure.

| | | | |
|---|---|---|---|
| PD1 | 0.00004 | -0.00061 | 0.00090 |
| CL1 | 0.18314 | 1.75704 | -1.51213 |
| CL2 | -0.72175 | -1.39634 | -1.71577 |
| S1A | -2.98663 | 2.21137 | 0.13009 |
| N1A | -5.82718 | -1.41809 | 0.04041 |
| N2A | -4.14974 | -0.18062 | -0.51840 |
| N3A | -5.64033 | 3.01898 | 0.77507 |
| C1A | -5.46903 | -0.34987 | -0.65658 |
| H1A | -6.12598 | 0.27195 | -1.24255 |
| C2A | -4.70971 | -1.94808 | 0.64995 |
| H2A | -4.76319 | -2.82884 | 1.26752 |
| C3A | -3.65366 | -1.17196 | 0.30376 |
| H3A | -2.60671 | -1.24027 | 0.56067 |
| C4A | -7.17768 | -1.95554 | 0.13362 |
| H4A | -7.46445 | -2.01943 | 1.18231 |
| H5A | -7.20495 | -2.94448 | -0.32266 |
| H6A | -7.85826 | -1.28875 | -0.39135 |
| C5A | -3.40071 | 0.90941 | -1.09162 |
| H7A | -3.96364 | 1.34257 | -1.91459 |
| H8A | -2.43237 | 0.54808 | -1.44426 |
| C6A | -4.56612 | 2.68752 | 0.49483 |
| S1B | 2.98736 | -2.21126 | -0.13166 |
| N1B | 5.82619 | 1.41955 | -0.04127 |
| N2B | 4.14937 | 0.18113 | 0.51737 |
| N3B | 5.64121 | -3.01758 | -0.77759 |
| C1B | 5.46861 | 0.35095 | 0.65542 |
| H1B | 6.12590 | -0.27073 | 1.24117 |
| C2B | 4.70838 | 1.94921 | -0.65049 |
| H2B | 4.76137 | 2.83017 | -1.26782 |
| C3B | 3.65272 | 1.17251 | -0.30442 |
| H3B | 2.60573 | 1.24043 | -0.56140 |
| C4B | 7.17643 | 1.95767 | -0.13429 |
| H4B | 7.46207 | 2.02461 | -1.18310 |
| H5B | 7.20394 | 2.94533 | 0.32475 |
| H6B | 7.85773 | 1.28954 | 0.38803 |
| C5B | 3.40109 | -0.90952 | 1.09037 |
| H7B | 3.96451 | -1.34264 | 1.91303 |
| H8B | 2.43259 | -0.54902 | 1.44346 |
| C6B | 4.56694 | -2.68662 | -0.49698 |
| CL1A | -0.18240 | -1.75838 | 1.51381 |
| CL2A | 0.72171 | 1.39533 | 1.71760 |

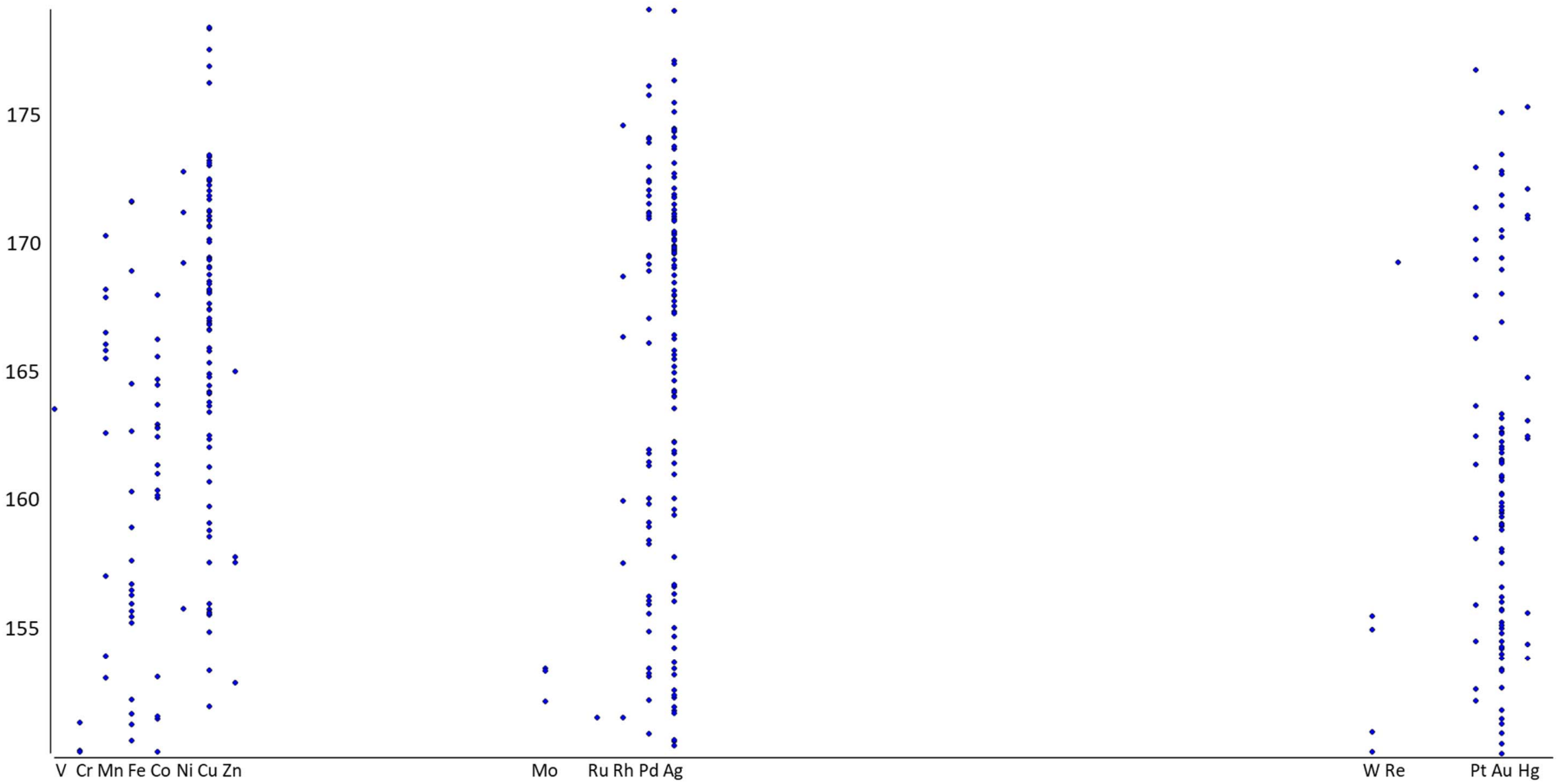


**Fig. S1**. The scatter plot of ∠(R–S···M)° (vertical axis, deg.) vs. metal atom type (horizontal axis) in crystals with intramolecular RS···M contact.

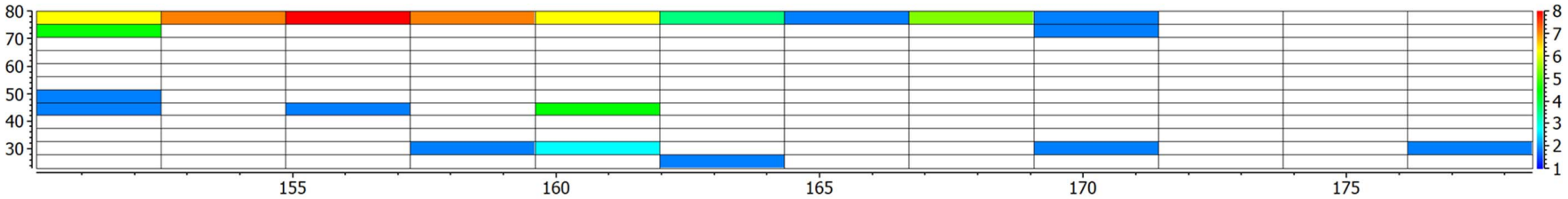


**Fig. S2**. The heat plot of the nucleus charge (vertical axis, *Ze*) of a metal atom vs. the RS···M angle (horizontal axis, *deg.*) in systems with intermolecular RS···M contacts. The cell color denotes distribution density.

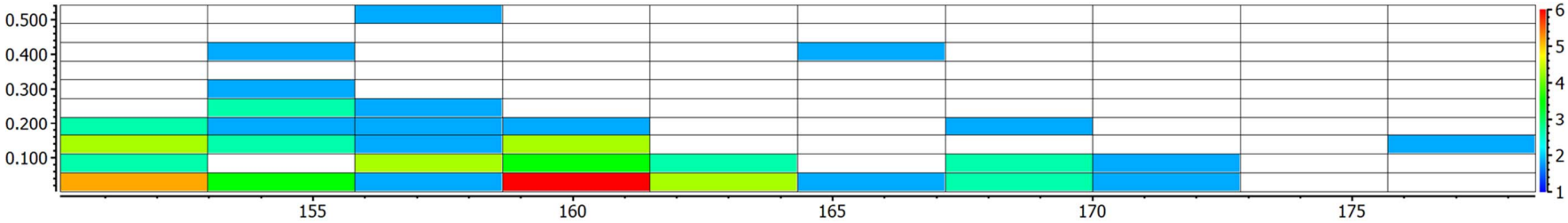


**Fig. S3**. The heat plot of the shortening of S···M distance with respect to appropriate $\Sigma R_{vdW}$ (vertical axis, Å) vs. ∠(R–S···M) angle (horizontal axis, *deg.*) in systems with intermolecular RS···M contacts. The cell color denotes distribution density.

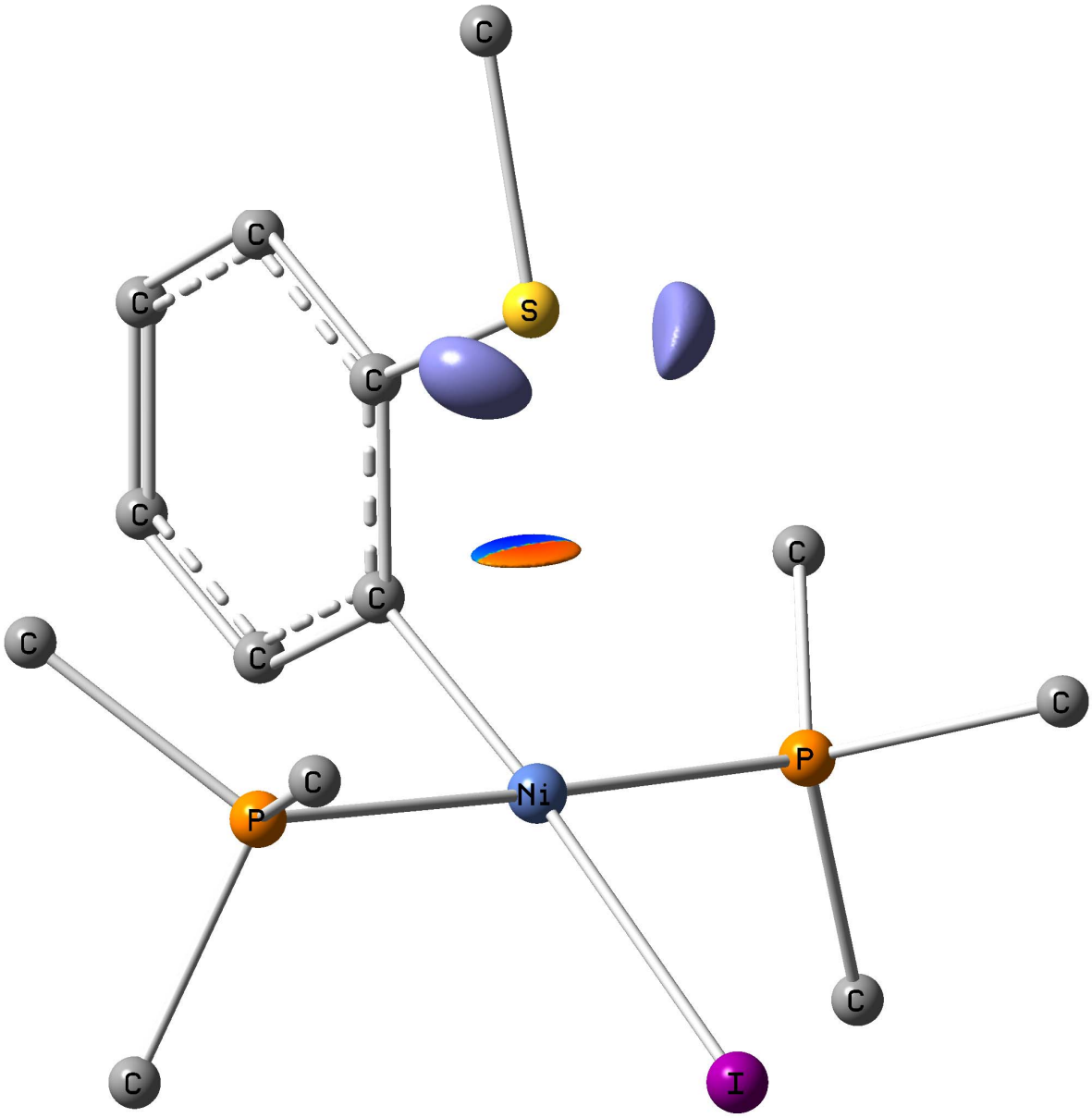


**Fig. S4**. The isosurfaces of selected real-space fields in the isolated equilibrium EGAXAN structure (H atoms were omitted for clarity): the RDG isosurface (0.25) in the middle of the Ni···S separation colored by the sign($\lambda_2$)·$\rho$(r) function (red color denotes negative values, blue color denotes positive ones), the ELF isosurface (0.95, violet spots) in the area of sulfur atom.

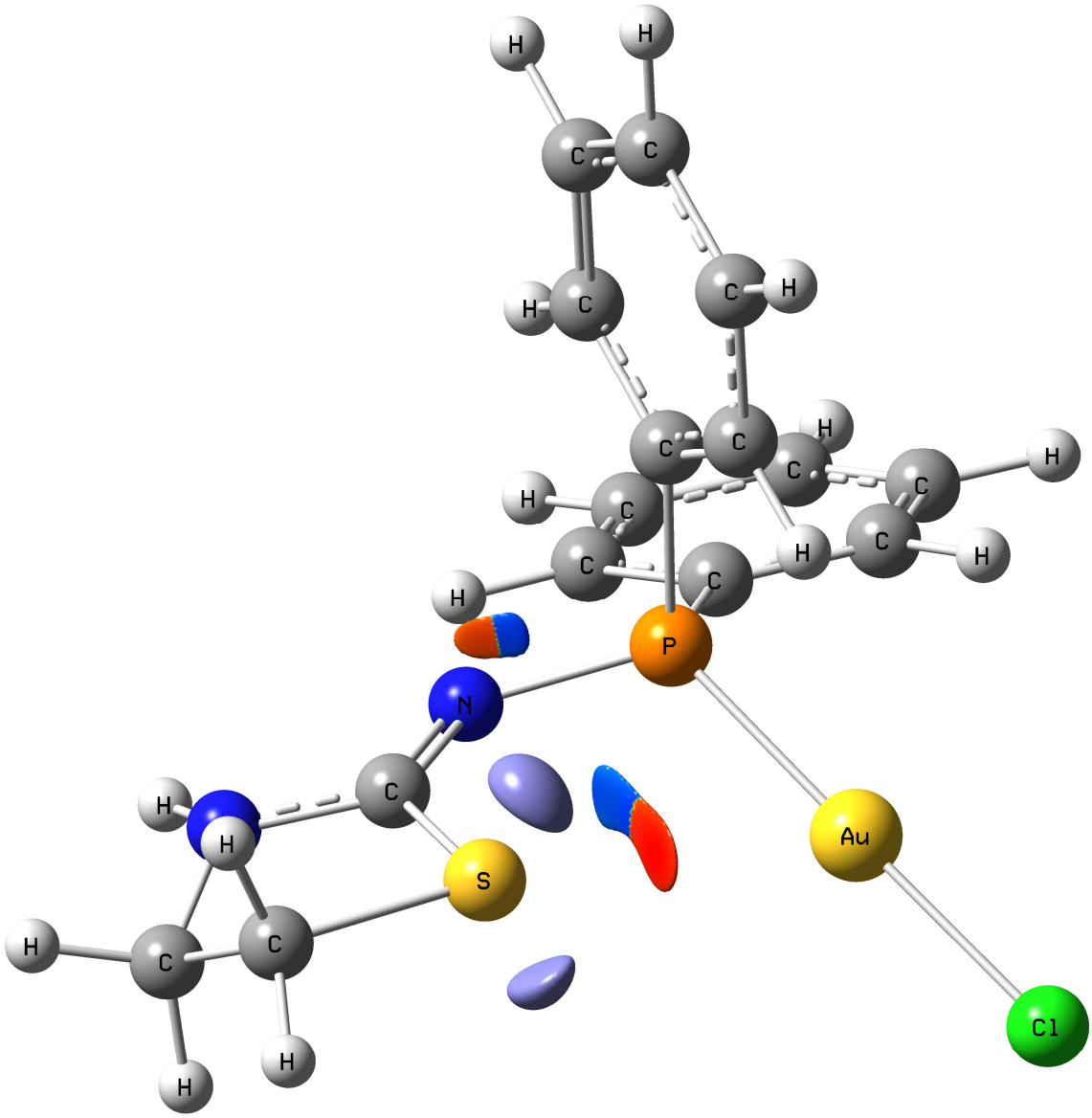


**Fig. S5**. The isosurfaces of selected real-space fields in the isolated equilibrium PAJDIP structure: the RDG isosurface (0.2) in the middle of Au···S and N···H separations colored by the sign($\lambda_2$)·$\rho$(r) function (red color denotes large negative values, orange color denotes small negative values, blue color denotes positive ones), the ELF isosurface (0.95, violet spots) in the area of sulfur atom.

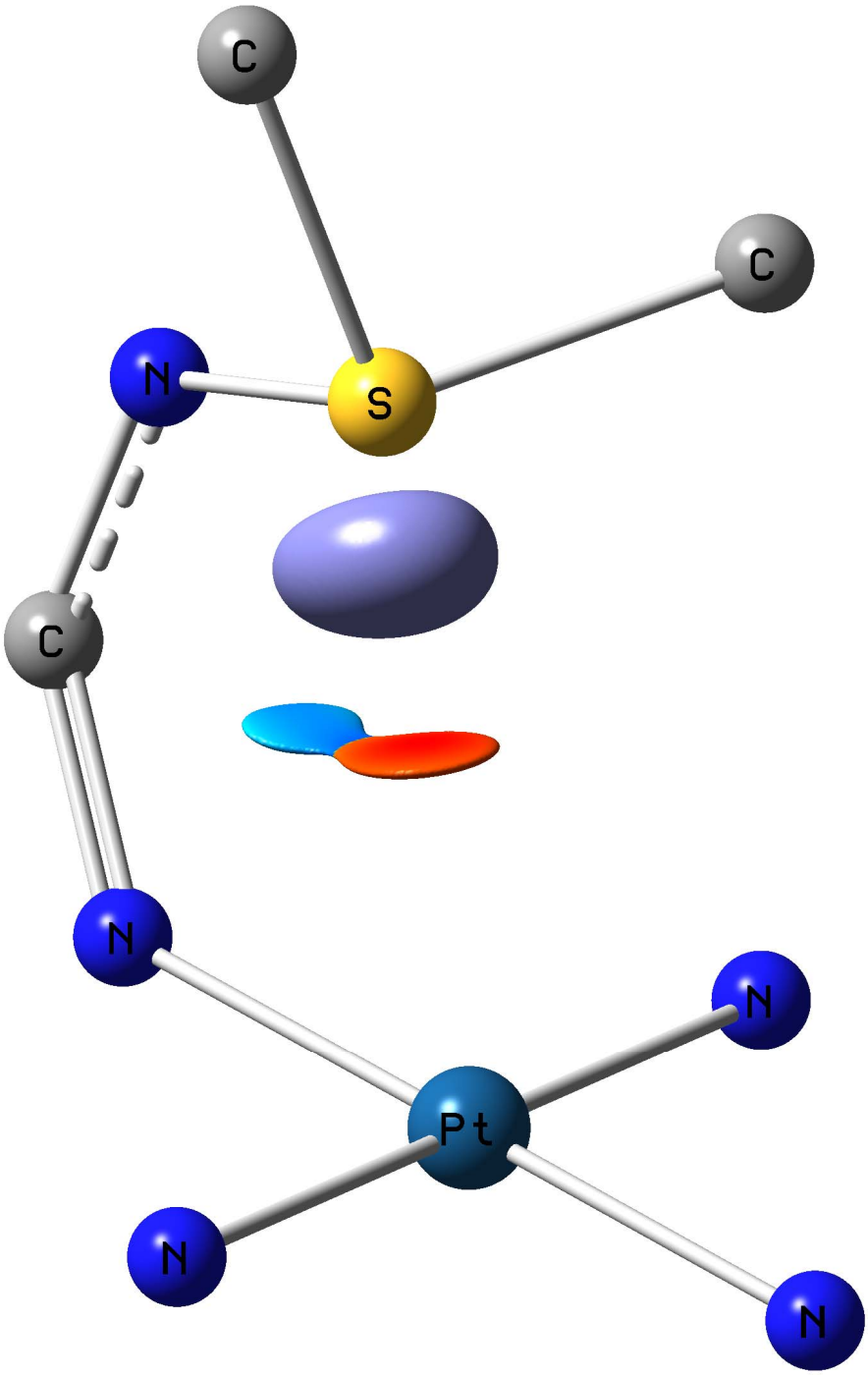


**Fig. S6**. The isosurfaces of selected real-space fields in the fragment of the isolated equilibrium WOVJOG01 structure: the RDG isosurface (0.2) in the middle of Pt···S separation colored by the sign($\lambda_2$)·$\rho$(r) function (red color denotes large negative values, blue color denotes positive ones), the ELF isosurface (0.95, violet spot) in the area of sulfur atom.

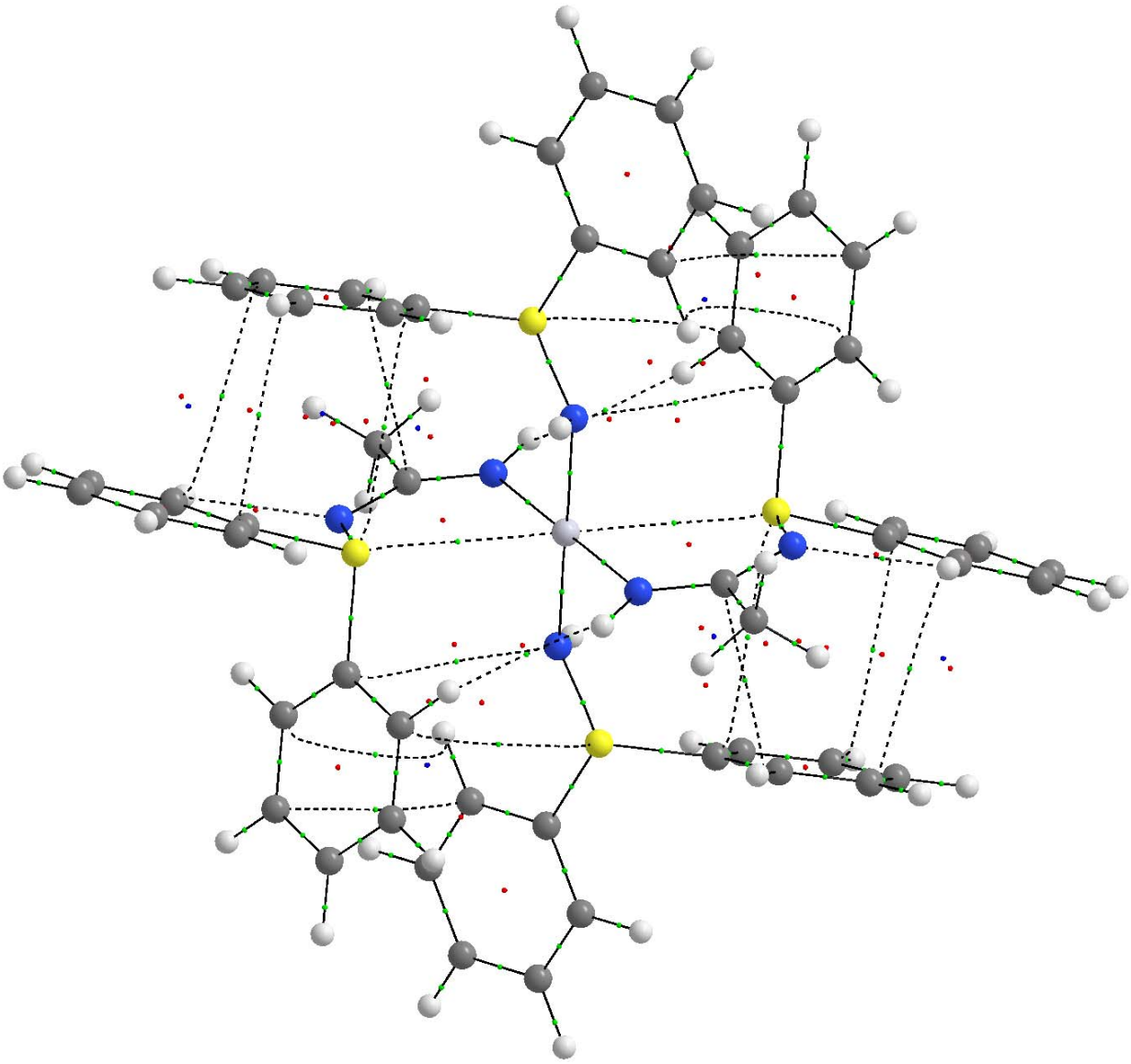

**Fig. S7**. The full atomic connectivity graph of the isolated equilibrium WOVJOG01 structure. The green, red and blue circles denote, respectively, (3, –1), (3, +1) and (3, +3) CPs of ρ(r). Bond paths of bonding noncovalent interactions are shown by dashed curves.

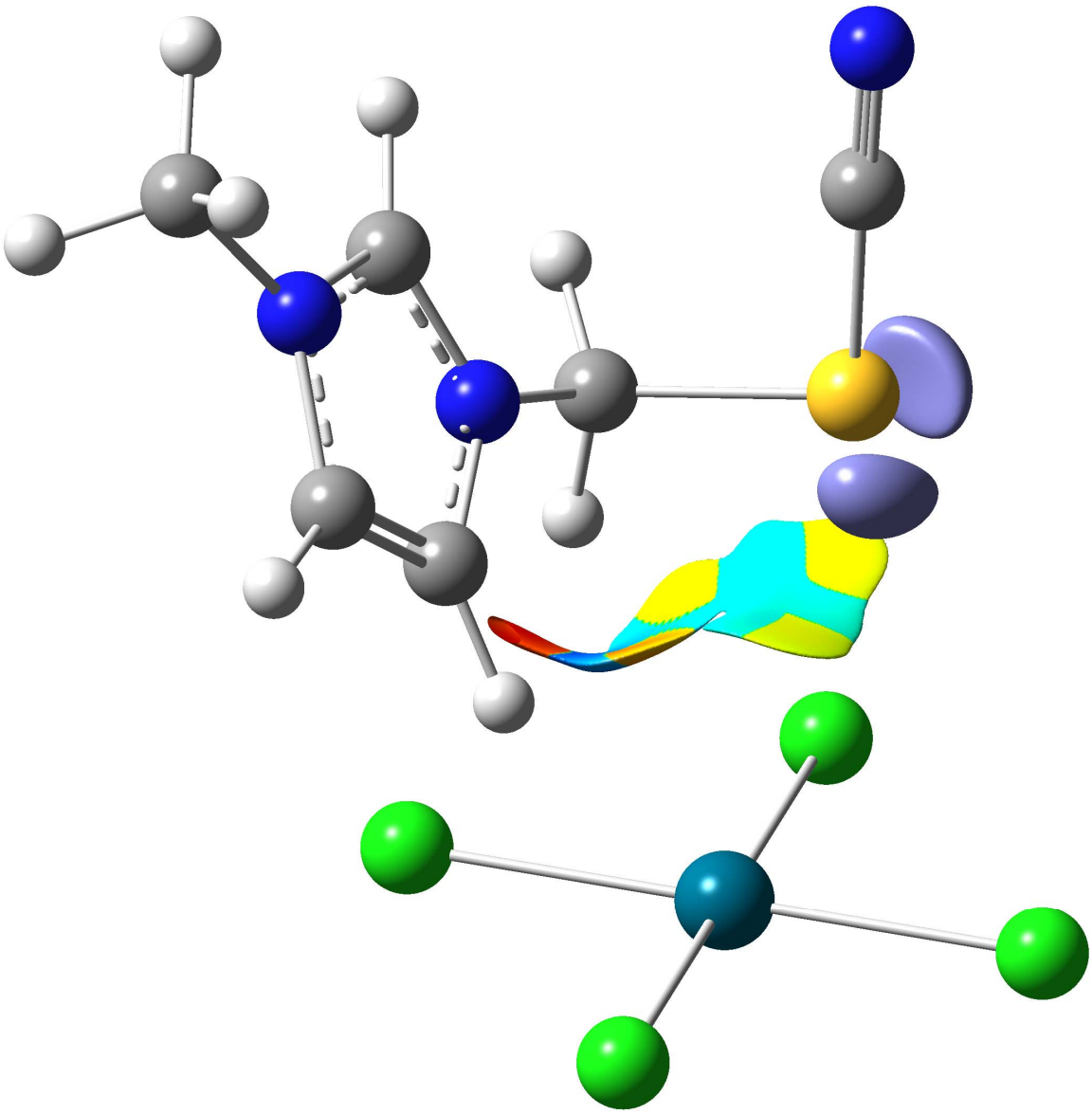

**Fig. S8.** The isosurfaces of selected real-space fields in the fragment of the isolated equilibrium CEWROM ionic pair: the RDG isosurface (0.2) between ions colored by the sign($\lambda_2$)·$\rho$(r) function (red color denotes large negative values, blue color denotes positive ones, light blue color denotes slightly positive values, yellow color denotes slightly negative values), the ELF isosurface (0.95, violet spot) in the area of the S atom.

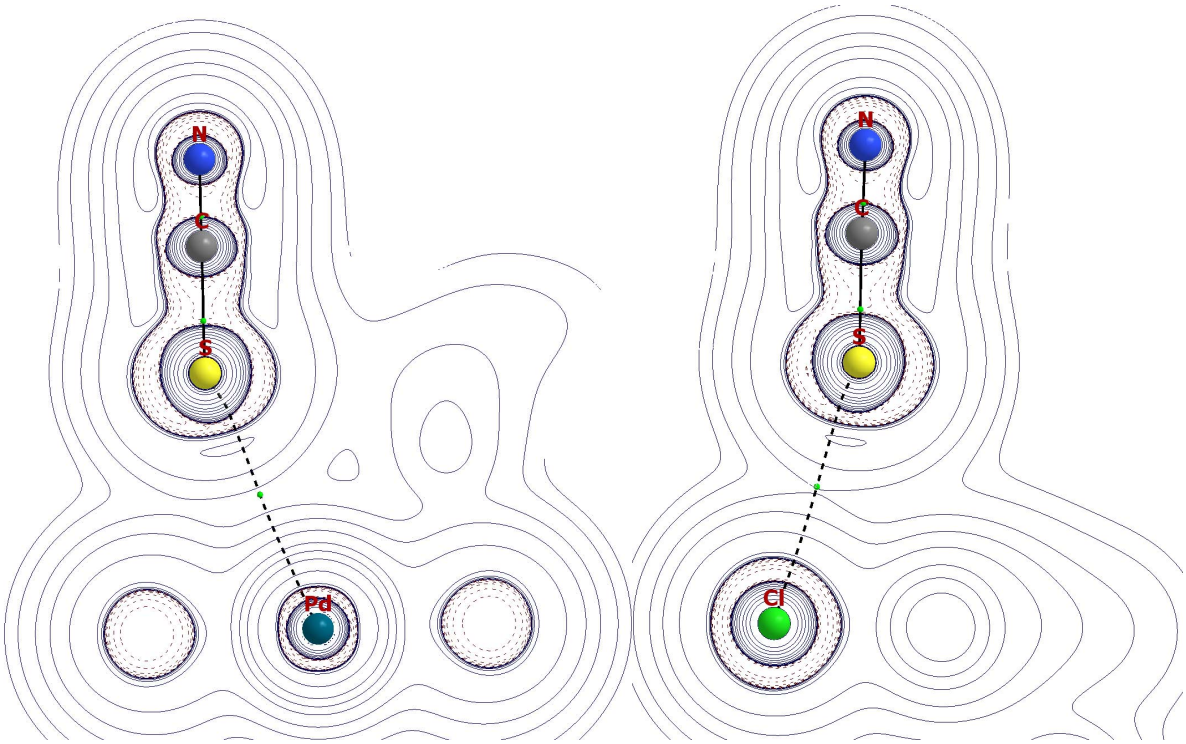


**Fig. S9.** The $\nabla^2\rho(r)$ contour plot in the C–S–Pd (left) and C–S–Cl (right) planes of the fragment of the isolated equilibrium CEWROM ionic pair (negative values are given by dashed lines). The green circles denote (3, –1) CPs of $\rho(r)$, while the bold dashed curves correspond to bond paths of bonding noncovalent interactions.

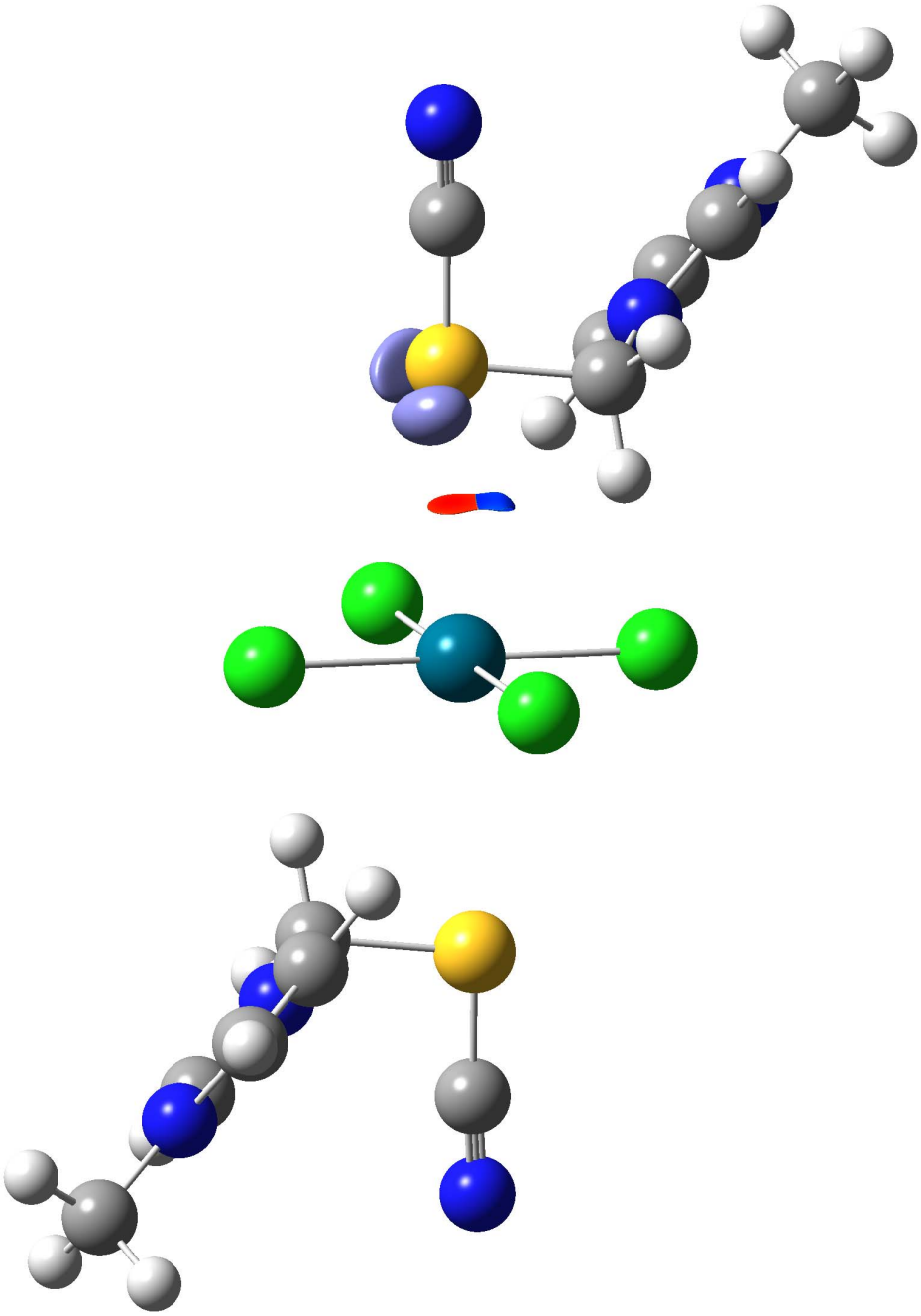

**Fig. S10.** The isosurfaces of selected real-space fields in the fragment of the isolated CEWROM ionic pair at crystal geometry: the RDG isosurface (0.2) between ions colored by the sign($\lambda_2$)·$\rho$(r) function (red color denotes large negative values, blue color denotes positive ones), the ELF isosurface (0.95, violet spot) in the area of sulfur atom.

Table S6. Some theoretical descriptors of RS···M interactions in the studied complexes.

| | $\rho(r)$, a.u.[a)] | $\nabla^2\rho(r)$, a.u.[a)] | $h_e(r)$, a.u. [a)] | Energy, kcal·mol$^{-1}$ [b)] | LP(S)→M CT, kcal·mol$^{-1}$ [c)] | d(M)→σ*(C–S) CT, kcal·mol$^{-1}$ [c)] |
|---|---|---|---|---|---|---|
| EGAXAN | No topological bonding | | | | –8.9 | –0.6 |
| PAJDOV | 0.013 | 0.031 | 0.0005 | 2.1, –1.9, –2.7 | –7.5 | –0.5 |
| PAJDIP | 0.016 | 0.039 | 0.0005 | –2.7, –2.5, –3.7 | –9.6 | –1.6 |
| WOVJOG01 | 0.022 | 0.052 | 0.0004 | –4.3, –3.6, –5.3 | –24.7 | –2.6 |
| CEWROM[d)] | 0.006 / 0.006<br>0.008 | 0.020 / 0.017<br>0.023 | 0.0008 / 0.0012<br>0.0010 | –1.7, –2.0, –2.7<br>. –1.2, –1.3, –1.8 | –7.6 / –0.7<br>–9.9 | –0.5 / –0.7<br>–1.2 |

a) At the corresponding CP (3,-1) of ρ(r), b) Interaction's energy estimations from, respectively, virial at CP, kinetic energy density at CP and ρ(r) surface integral, c) the second-order perturbation theory analysis within the NBO scheme d) the data are given for the equilibrium complex (two CPs corresponding to the RS···Pd/RS···Cl interactions) and for the crystal geometry (only the RS···Pd CP).