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Electronic Supplementary File for manuscript: π-hole spodium bonding in tri-coordinated Hg(II) complexes

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Theoretical methods

The calculations were performed using Gaussian-16 program[1] at the PBE0-D3/def2-TZVP level of theory using the X-ray coordinates. The Grimme's D3 dispersion correction has been used in the calculations.[2] The molecular electrostatic potential surfaces have been computed at the same level of theory. This level of theory has been successfully used before to investigate SpB interactions.[3] The QTAIM analysis[4] and NCIplot index[5] calculations have been computed at the same level of theory by means of the AIMAll program.[6]

Table S1. CSD reference codes of HgXPn2, HgXCh2; HgXHa2 X-ray structures

$HgXPn_2$; total number of hits: 66				
BEFLIH	BZAMHG	BZPYHG	CAZTII	ECURUR
EFUDOY	ENTIHG	FINFIR	FOLLAT	GEQREZ
GIHYOL	HASTOK	HESMAT	HOSCOH	HOXBUR
HOXCAY	HOXCEC	IFUHEW	IRIZIU	IRIZOA
IZIDUQ	JEJGOU	JUWNOE	KAZYEP	KIHWIH
KIKBIP	KOLCOE	LEGKUD	LEGPOD	LUWCEM
LUWCIQ	LUWCUC	MBPYHG10	MEPHGC10	MNAZHG
MPYHGA	MPYHGA10	NAPRHG	ODUPIN	PAVTAH
PHNAHG	PIXVAU	QOTLOA	QUKDUW	ROBYEN
SEGSEE	SEQMIL	SEQMOR	SEQMUX	SEQNIM
SIRDEC	SUTTEG	TAWYEV	TITBUT	TUSVAG
TUTLAX	TUTLEB	TUTLIF	UJIKON	VOCVEO
WOLYEB	XETXUQ	XULREC	YIZPIH	ZAXXUT
ZOWROS				
$HgXCh_2$; total number of hits: 147				
ABOGAZ	ACHGPT	ACHGPT10	AJAJAX	AROVOT
BEMNOY	BOBZUO	BOCBAX	BOCBEB	BOMVAA
CECSIN	CHMEHG	CUBVEB	DEFBEV	DELFIJ
DIBWOA	DOJFUE	DOLFAM	DPSEHG	DPSEHG01
DUFQOK	DUVLUC	EBUSUR	EDIDEB	EDUCUB
EDUDAI	EDUDEM	EGIDOQ	EGIDUW	EKIYON
EKIYUT	EYAYUY	FAKCOL	FAKHOR	FETTUT
FINJOD	FODRUN	GEJTOF	GERLOG	GERLUM
GEZPEG	GOKPIG	GUVQUJ	HGCSUR01	HUBRON
HUTZIF	IMUFUR	IMUGAY	ITASUR	JANZOQ
JEFVIZ	JUWFOW	KAHKAI	KELVUS	KEXZOC
KEYMOQ	KINZAI	KIQSAE	KIVVAM	KIVVIU
KUKQUE	KUKSAM	LAJCIJ	LAJGOV	LATTEF
LECDED	LOLYAM	LOLYEQ	LULVIX	MEDTHG
MIKKAT	MIYPUG	MTACHG	NASLID	NEGREZ
NEGRID	NEJGIV	NOPTUI	NOPVIX	NOPVOD
NOSSIX	NOSSUJ	NOYNIY	PAFXOJ	PETFUP
PETFUP10	POCFAP	POTJAK	PTEHGP	QABJEI
QEHDIQ	QITKIQ	QOHZAO	RACJOW	RASGIC
RICLUK	SANQAZ	TASZOD	TECKAN	TECKIV
TOBLIF	TPARHG10	TUJFUZ	TUJFUZ01	TUJFUZ02
UCEYAD	UDANAO	UDEDUF	UPITIY	UPITOE
UPITUK	UPIVAS	VANFAT	VIMBEA	VIYKUK
VIYLAR	VIYLIZ	VIYLOF	VOXTOR	VUKLOD
WAPFOK	WEJCUM	WEWREY	XAKHOG	XOBQAI

XOLGOW	XUHROI	XUHROI01	YARNIP	YAXHEN
YAXHIR	YEYYUX	YEYZEI	YOLHUD	YOLJAL
YOLJEP	YOMXIJ	YOMXOP	YOMXUV	YOMYAC
ZESCUV	ZESDAC	ZETKAK	ZIWDUG	ZUHZOT
ZUHZUZ	ZURXEP			
$HgXHa_2$; total number of hits: 181				
AFEYOZ	AXAWON	BABLOH	BABNAU	BARGUW
BEHLUV	BETPEV	BHGIRP	BIMJAI	BITHIV
BOLLET	BOPXIN02	BORYIC02	BORYIC03	BSHGCL
BUKYEN	BUKYIR	CAGPIK	CEKHOR	CEKJEJ
CEKJIN	CHGIRP	CIBDUN	CIDLIM	CIDZUL
CINZEF	CMSMOM	COZMAF	COZMAF10	CPCOHG10
CPRUHG	CUFCEL	CUFCEL10	CUPXUH	DEBWAJ
DEFYET	DEJZIB	DILTOH	DOBCAZ	DOBCIH
DOTLIH	DTIZHG01	DTIZHG10	DUGCEN	DUSFAA
ELEWEY	EMIFOX	EMINOF	EMINUL	EMSCHG
ENTIHG	EWOREN	EXERII	FEGLAE	FIJQOF
FOCLOY	GARSEX	GIRPUU	GIRQAB	GOCTUQ
GOGHUH	GUBBEK	HARRAV	HGCBPO10	HGCETS
HGCQIN	HIRTUX	HOTCEA	IBAFEY	IBAFIC
ICACUN	IRUVEW	JANFEK	JOGJOE	KEZBAT
KIQKED	KOFXAE	KOZREY	KOZREY01	KUKNAF
LAQGIT	LEHGAI	LEQRAB	LEQRUV	LITSEM
LOMPAG	LOWJUE	MAJHAI	MAJHEM	MHPCHG
MIXQIW	MOLVUE	MOWFUA	MOWGAH	MUMDAB
NEHQUM01	NOFJIE	NOSSUJ	OXTETH10	PASCHI
PAYCAT	PERGOJ	PEWVAO	PIGRIH	PURGIS
QEMDUH	QEMDUH01	QEVHUU	QEZNUG	QEZPAO
QEZPIW	QEZPOC	QEZPUI	QEZQAP	QIJXIQ
QIJXIQ01	QOFQEH	QOFQEH01	QQQBVJ	QQQBVJ02
QQQBVJ03	QQQBVJ04	QQQBVJ31	QQQBVJ32	QQQBVJ33
RAFJUD	REGVUV	RICSIG	RIMKUW	RITMAI
RORREV	RUYVUE	SARBOC	SEBNAP	SIFCAL
SIRMAH	SODZES	SOYPIF	SURNOI	TABYUS
TAGCAF	TEBPAS	TEBPEW	TMAHGB	TMSCHG
TMSHGI	TMSHGI01	TMSHGI02	TOCJIH	TOCJON
UCEYIL	UGUBOO	UGUQES	UJEROQ	UJEROQ01
UYOCES	UYUSUD	VEGSAD	VEQJAE	VEWKOY
VICFIW	VOFROX	VOZGEW	VUDSUJ	VUJYUV
VUPWUZ	WABCEH	WIVTAY	WURPIJ	WURPOP
XIVKIW	XIVKOC	XOGKIN	XUVRIQ	YARNEL
YAWNUF	ZUPCUI	ZZZDWQ	ZZZHBA	ZZZTLW
ZZZTOE				

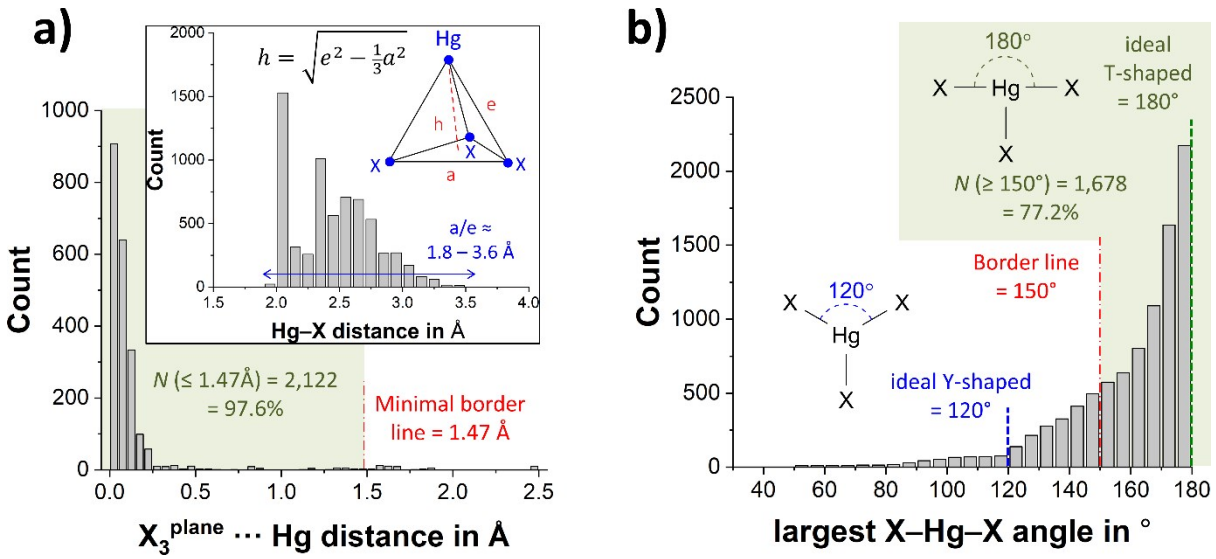

Figure S1. Plots to assess the geometry of HgX_3 structures in the CSD. (**a**): Plot of the hit-count as a function of the $X_3^{plane}\cdots Hg$ distance to assess the planarity of HgX_3 structures. The plot shows that nearly all structures (97.6%, green) are best considered as planar, as opposed to a triangular pyramidal structure. The inset figure shows the relationship between the height of a triangular pyramid (h) and length of the edges (a and e), together with the actual distribution of Hg–X distances. Assuming that a = e = Hg–X, these give a height in between 1.47 and 2.94 Å. The lower value of 1.47 Å is used as borderline between a planar and triangular pyramidal structure (indicted in red). (**b**): Plot of the hit-count as a function of largest X–Hg–X to assess the proportion of structures with Y-shaped (∠ = 120° in the ideal case) or a T-shaped (∠ = 180° in the ideal case) geometry. The border between the two structures of 150° ((120+180)/2) is marked with the red dash-dot line.

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