Modeling molecular crystals formed by spin-active metal complexes by atom-atom potentials: Electronic Supplementary Information

Anton V. Sinitskiy[*]

Poncelet Laboratory, Independent University of Moscow,

Bolshoy Vlasyevskiy Pereulok 11, 119002, Moscow, Russia

Andrei L. Tchougréeff[†]

Poncelet Laboratory, Independent University of Moscow,

Bolshoy Vlasyevskiy Pereulok 11, 119002, Moscow, Russia and

JARA, Institut für Anorganische Chemie,

RWTH Aachen, Landoltweg 1, 52056 Aachen, Germany

Andrei M. Tokmachev and Richard Dronskowski

JARA, Institut für Anorganische Chemie,

RWTH Aachen, Landoltweg 1, 52056 Aachen, Germany

I. The shortest atom-atom contacts (we selected those separated by less than the sum of the corresponding van der Waals radii) in the crystals studied are given in Tables I-III and depicted on Figs. 1-3.

II. To study the influence of the interaction parameters on the equilibrium configurations of the crystals, we optimized the crystals of $Fe(btz)_2(NCS)_2$ with the interaction parameters slightly modified. We increased, one by one, parameters for each pair of atoms (the well depth and the equilibrium separation) by 5% to estimate numerically the sensitivity of the energy contributions to the potential parameters. The choice of the $Fe(btz)_2(NCS)_2$ crystals was suggested by the fact that it is poorly described with the original parameterization. Changes in the optimal lattice parameters δa, δb, δc, caused by 5% variations of each parameter of the atom-atom interaction energy, are given in Table IV. The table also specifies

———

[*]Electronic address: `sinitsk@mail.ru`
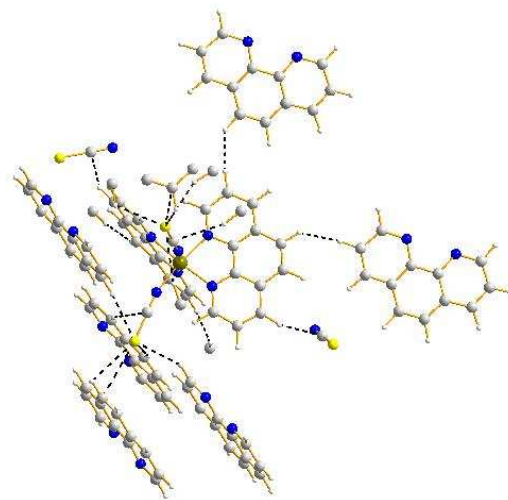
[†]Electronic address: `andrei.tchougreeff@ac.rwth-aachen.de`

FIG. 1: Contacts in the crystal of $Fe(phen)_2(NCS)_2$.
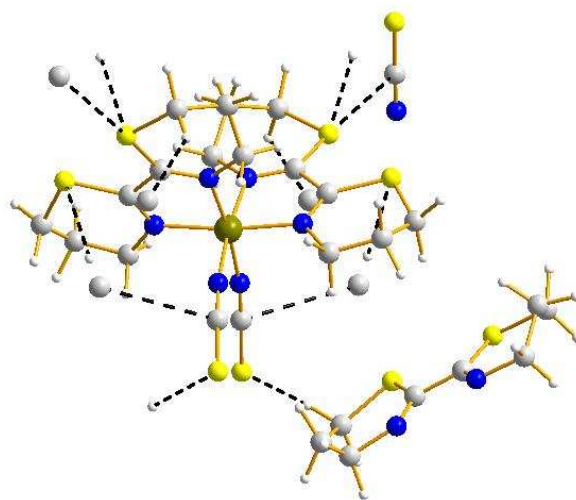

FIG. 2: Contacts in the crystal of $Fe(btz)_2(NCS)_2$.

the differences between the experimental values of the lattice parameters and those calculated with the initial parameters of [36] (exp.). The table shows that most of the interaction parameters very slightly affect the optimal configuration of the crystals. Corrections caused by *the well depth* changes by 5% are a hundred times smaller than the difference between the experimental and calculated lattice parameters, leaving no hope to reduce the discrepancy by fitting the well depths within reasonable frames. The same applies to most of the
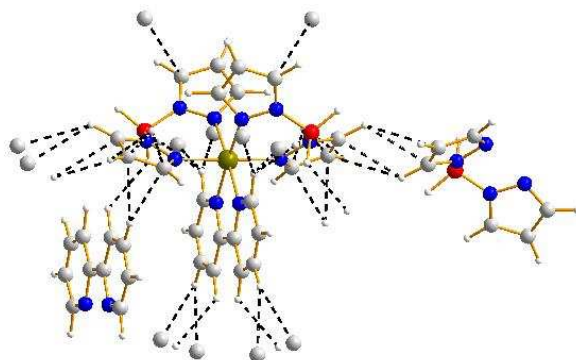
FIG. 3: Contacts in the crystal of Fe(bpz)$_2$(bipy).

TABLE I: Shortest intermolecular contacts in the LS and HS crystals of Fe(phen)$_2$(NCS)$_2$: interatomic distances (Å) determined experimentally (exp.) or calculated with (6-12) and (6-exp) potentials and the sum of the van der Waals radii (vdW) of the atoms [36].

Pair	R(exp.)	R(vdW)	R(6-12)	R(6-exp)
The LS isomer				
C−H$\cdots$H−C	2.093	2.34	2.374	2.289
S$\cdots$C	3.314	3.55	3.370	3.341
C$\cdots$H−C	2.589, 2.784	2.92	2.620, 2.801	2.520, 2.866
S$\cdots$H−C	2.832, 2.891,	2.97	3.162, 3.311,	3.185, 3.419,
	2.911, 2.951		3.052, 2.907	2.983, 2.915
The HS isomer				
C−H$\cdots$H−C	2.211	2.34	2.411	2.307
S$\cdots$C	3.357	3.55	3.345	3.339
C$\cdots$H−C	2.570, 2.750	2.92	2.635, 2.872	2.509, 2.792
S$\cdots$H−C	2.941	2.97	3.121	3.156

TABLE II: Shortest intermolecular contacts in the LS and HS crystals of $Fe(btz)_2(NCS)_2$: interatomic distances (Å) determined experimentally (exp.) or calculated with (6-12) and (6-exp) potentials and the sum of the van der Waals radii (vdW) of the atoms [36].

Pair	R(exp.)	R(vdW)	R(6-12)	R(6-exp)
The LS isomer				
S$\cdots$C	3.275	3.55	3.352	3.333
S$\cdots$H$-$C	2.706, 2.743, 2.942	2.97	2.886, 2.840, 2.849	2.755, 2.741, 2.907
C$\cdots$H$-$C	2.811	2.92	2.931	2.805
C$\cdots$C	3.453	3.50	3.668	3.570
The HS isomer				
S$\cdots$C	3.351	3.55	3.401	3.384
S$\cdots$H$-$C	2.893, 2.925	2.97	2.832, 2.904	2.770, 2.805
C$\cdots$H$-$C	2.848, 2.888	2.92	2.802, 2.851	2.693, 2.755

atom-atom equilibrium separations on the corresponding interaction energy curves (C$\cdots$C, H$\cdots$H, N$\cdots$N, N$\cdots$H, *etc.*), though in this case the changes in the lattice parameters caused by a 5% increase of the distances are only tens times smaller than the required scale of correction. Only three parameters significantly affect the optimal structure of the crystal: the equilibrium separations for the S$\cdots$C, S$\cdots$H, and S$\cdots$S pairs.

TABLE III: Shortest intermolecular contacts in the LS and HS crystals of Fe(bpz)$_2$(bipy): in-teratomic distances (Å) determined experimentally (exp.) or calculated with (6-12) and (6-exp) potentials and the sum of the van der Waals radii (vdW) of the atoms [36].

Pair	R(exp.)	R(vdW)	R(6-12)	R(6-exp)
The LS isomer				
C⋯H−C	2.655, 2.658, 2.689, 2.817, 2.879, 2.912	2.92	2.732, 2.716, 2.815, 2.877, 2.895, 2.811	2.651, 2.606, 2.720, 2.763, 2.835, 2.818
C−H⋯H−C	2.332	2.34	2.390	2.333
C−H⋯H−B	2.283	2.34	2.445	2.301
C⋯C	3.368, 3.374	3.50	3.327, 2.720	3.387, 3.412
The HS isomer				
C⋯H−C	2.579, 2.719, 2.782, 2.813, 2.878, 2.900	2.92	2.728, 2.739, 3.002, 2.809, 2.838, 3.189	2.622, 2.657, 2.892, 2.707, 2.769, 3.040
C−H⋯H−B	2.318	2.34	2.477	2.336
C⋯C	3.360, 3.420	3.50	3.250, 3.304	3.194, 3.236
N⋯H−C	2.606	2.67	2.786	2.642

TABLE IV: Changes in the optimal lattice parameters a, b and c (10^{-4}Å) of Fe(btz)$_2$(NCS)$_2$ caused by 5% increase of the (6-exp) potential parameters.

Pair	The LS isomer			The HS isomer			The HS/LS difference		
	δa	δb	δc	δa	δb	δc	$\delta \Delta a$	$\delta \Delta b$	$\delta \Delta c$
well depth									
H$\cdots$H	12	14	-3	28	-1	-5	16	-15	-2
C$\cdots$H	-14	-11	1	6	-9	11	20	2	10
N$\cdots$H	-13	-5	-13	-15	-6	-13	-2	-1	0
S$\cdots$H	126	24	6	85	41	-10	-41	17	-16
C$\cdots$C	-28	-20	-19	-27	-20	-14	1	0	5
N$\cdots$C	-25	-10	-31	-29	-12	-27	-4	-2	4
S$\cdots$C	-25	27	51	-11	18	31	14	-9	-20
N$\cdots$N	-11	-4	-1	-13	-4	3	-2	0	4
S$\cdots$S	-23	-13	4	-26	-8	19	-3	5	15
equilibrium distance									
H$\cdots$H	251	216	5	483	24	-33	232	-192	-38
C$\cdots$H	396	98	365	755	74	421	359	-24	56
N$\cdots$H	-60	-29	-48	-41	-23	-21	19	6	27
S$\cdots$H	2084	828	700	1741	991	533	-343	163	-167
C$\cdots$C	168	-55	269	277	-61	263	109	-6	-6
N$\cdots$C	-148	-83	-70	-137	-90	-2	11	-7	68
S$\cdots$C	714	1131	2075	894	958	1821	180	-173	-254
N$\cdots$N	-80	-27	271	-109	-18	305	-29	9	34
S$\cdots$S	11	-58	1116	-22	28	1226	-33	86	110
exp.	705	2930	1354	2098	1843	1131	1393	-1087	-223