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SUPPLEMENTARY MATERIAL TO

Derivation of a new set of force field parameters for ammine complexes of chromium(III) containing halogeno ligands: modeling of the *trans*-influence of halogenido ligands

IVANA DJORDJEVIĆ[1], SONJA GRUBIŠIĆ[1]*, MILOŠ MILČIĆ[2] and SVETOZAR NIKETIĆ[1]

[1]*Center for Chemistry, ICTM, University of Belgrade, Njegoševa 12, 11001 Belgrade, Serbia and* [2]*Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11001 Belgrade, Serbia*

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TABLE S-I. Additional VOFF parameters for $[Cr(NH_3)_5X]^{2+}$ (X = F, Cl, Br, I) series; r_0 and θ_0 are the equilibrium bond length and bond angle, respectively; k_r and k_θ are the force constants for the bonds and bond angles, respectively (1 kcal = 4.184 J)

Bond stretching	k_r / kcal mol^{-1} Å^{-2}		r_0 /Å	
M–F	310		1.883	
M–Cl	160		2.300	
M–Br	170		2.400	
M–I	200		2.620	
Angle bending	k_θ / kcal mol^{-1} rad^{-2}		θ_0 / rad	
	cis	*trans*	*cis*	*trans*
N–M–N	30.00	30.00	1.570	3.142
N–M–F	15.00	15.00	1.570	3.142
N–M–Cl	20.00	20.00	1.570	3.142
N–M–Br	30.00	30.00	1.570	3.142
N–M–I	35.00	35.00	1.570	3.142
van der Waals	ε / kcal mol^{-1}		r^* / Å	
F···H	0.095		3.40	
F···N	0.100		3.70	
Cl···H	0.106		3.53	
Cl···N	0.115		3.85	
Br···H	0.122		3.68	
Br···N	0.133		4.00	
I···H	0.136		3.83	
I···N	0.150		4.10	

* Corresponding author. E-mail: grubisic@chem.bg.ac.rs

TABLE S-II. Comparison of the calculated partial atomic charges (esu); key: *q* = partial atomic charges, eq = equatorial or *cis*(X,NH_3), ax = axial or *trans*(X,NH_3), X=F, Cl, Br, I; Methods (as cited in the original publications): NPA = natural population analysis, MKS = Merz–Kollman–Singh scheme, NLDA = nonlocal density approximation, MEP = molecular electrostatic potential

Complex	*q*(M)	*q*(N)	*q*(H)	*q*(F)	*q*(Cl)	*q*(Br)	*q*(I)	Meth.	Ref.
Published data									
$[Co(NH_3)_6]^{3+}$	1.67	–1.19	0.47					NPA	1
$[Co(NH_3)_6]^{3+}$	1.55	–1.05	0.43					MKS	1
$[Co(NH_3)_6]^{3+}$	2.0								2
$[Co(NH_3)_6]^{3+}$	2.71								3
$[Co(NH_3)_5F]^{2+}$	1.6								2
$[Co(NH_3)_5F]^{2+}$	1.76								3
$[Cr(H_2O)_6]^{3+}$	1.403							NLDA	4
$[Cr(H_2O)_6]^{3+}$	0.722							MEP	4
$[Cr(H_2O)_6]^{3+}$	2.12								5
$[Cr(H_2O)_6]^{3+}$	2.2								2
$[CrF_6]^{3-}$	1.62							NPA	6
$[ZrF_6]^{2-}$	2.634			–0.77				MEP	7
$[ZrCl_6]^{2-}$	1.509				–0.58			MEP	7
$[ZrBr_6]^{2-}$	0.938					–0.49		MEP	7
$[ZrI_6]^{2-}$	0.440						–0.41	MEP	7
This work									
$[Cr(NH_3)_5F]^{2+}$	1.63	-1.01^{eq}	0.41^{eq}	–0.60					
$[Cr(NH_3)_5Cl]^{2+}$	1.13	-0.88^{eq}	0.38^{eq}		–0.44				
$[Cr(NH_3)_5Br]^{2+}$	0.77	-0.77^{eq}	0.35^{eq}			–0.34			
$[Cr(NH_3)_5I]^{2+}$	0.48	-0.59^{eq}	0.30^{eq}				–0.22		

CSD REFCODES

For structures with Cr–F bonds

ADOSOC, BAPPOX, BAVGOU, BAVGUA10, BIVVUX, BORWOU, BORWUA, BORWUA01, BUTDAV, DAFHOH, DEDCAQ, DIYFEW, DORZEP, DUCQIC, DULQAD, FEZXUD, FOJBAH, GAWBUC, IZOVEZ, KOMREJ, LEYDOJ, LEYDUP, LEYSEN, MPZFCR, OCOLIB, POFGEX, PUXPUT, QEXSES, SIXWOL, SUKHAH, TAZFCR, TETVUK, VAFDEN, VAFDIR, VIWMEU, VOLREU, YASHAB, YASHOP.

For structures with Cr–Cl bonds

ABILUT, AMZCCR, BIJZOK, BIWPIH, CEDCRC, COKJAN, CUKPON, CUSBUN, DOHBEH, EGULOI, EKOCEM, EMIWIG, EMUNIJ, FAMVUK10, FUHCIU, GADTOU, JAQPEW, JATTED, JATVAB, JOFYIM, JOFYOS, JOMNAA, JOMNAA01, JOMNEE, KUGMAA, KUGMEE, LIJRAX, MATHIZ, MATHOF, MATHUL, MOLPUZ, PADSIW, PAZDUQ, PUWFAO, PYMECR, QISXIA, QOWZOS, QOWZUY, QOXBAH, RAKGIT, RUNRIB, RUNRIB01,

TEBDIO, TEZSIA, TEZSOG, TEZSUM, TEZTAT, TEZTEX, ULAYUC, UWEKEN, WATREO, WOGRUG, YISLIV, YISLOB, ZALZER, ULAYUC01, WEBCAJ, ACUCAE.

For structures with Cr–Br bonds

BIWBEO, BOGDIL, CAGCIW, ESIMUO, IHEJOU, KUGMEE, MAMLER, PUDNUY, PUDPAG, PURCIO, UKEDEU, UKEDIY, VAGBIQ, VAQFAU, VAVNOV, VEFVEH, YIBWOV, TEDYIM.

For structures with Cr–I bonds

BOGDOR, CPMINC, DAGNUW, JEKKEP, NATZIS, NMCPNC, ODAXIA, OFAKAI, PPNCCO, RAJXUV, SESYAQ, UGUBAZ, UKEDOE, UKEDUK, UKEFAS, UKEFOG, UKEFUM, VAZWAU, YEKLUW.

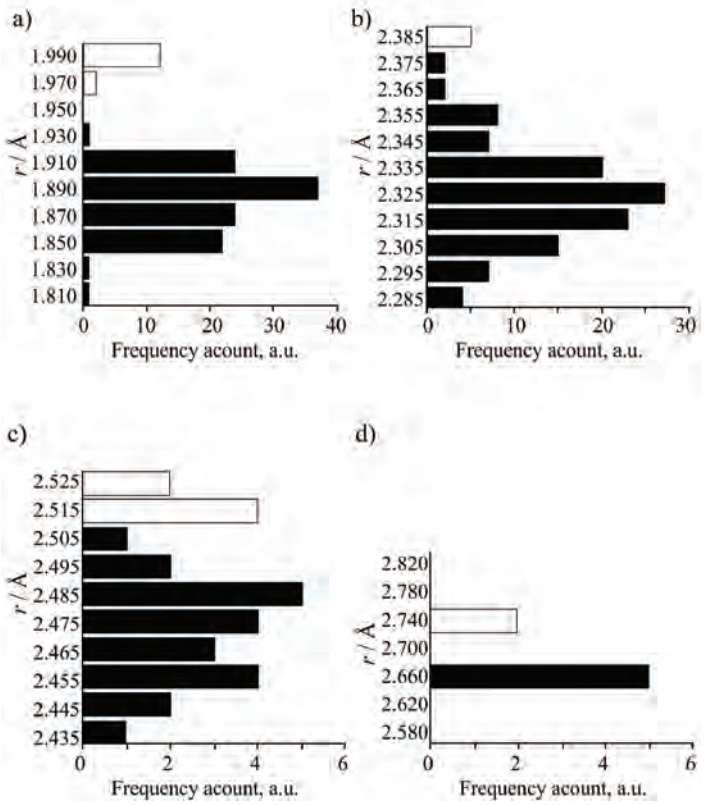

Fig. S-1. Distribution of chromium(III)–halogen distances in the crystal structures retrieved from CSD (2013.): a) for Cr–F bond lengths (Å); b) for Cr–Cl bond lengths (Å); c) for Cr–Br bond lengths (Å) and d) for Cr–I bond length (Å). The data used in the derivation of the statistics are shown in black; data eliminated for any reason (see text) are shown in white. Note the difference in the scale for the *x*-axis between the upper and lower pair of charts.

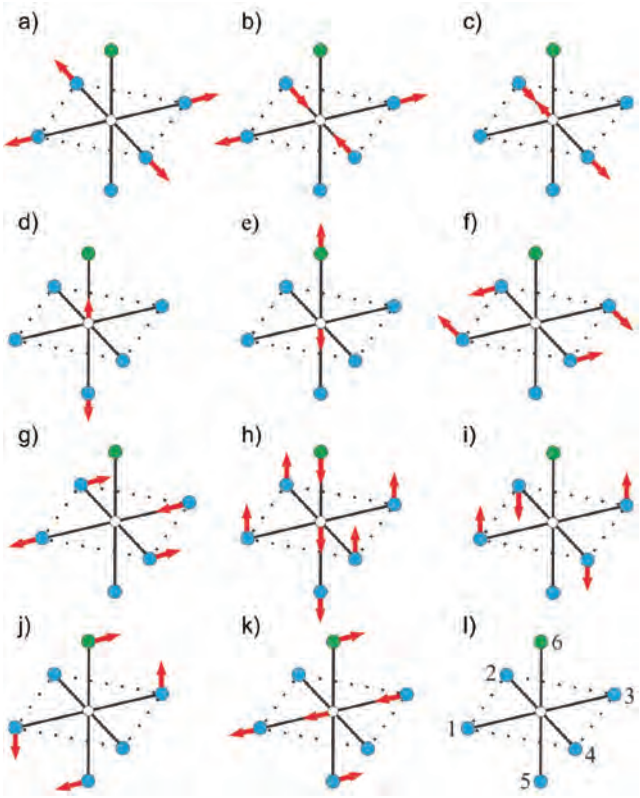

Fig. S-2. Symmetry coordinates for the normal vibrations of the C_{4v}-[CrN_5X] skeleton. Definition of internal coordinates for skeletal vibrations: Metal–ligand bonds: R_i (i = 1,6). Octahedral angles: α_{ij} (i, j = ligand atoms). a) $S_1(A_1)$ $\phi_1(A_1) = (1/2)\Delta(R_1 + R_2 + R_3 + R_4)$, b) $S_2(B_1)$ $\phi_2(B_1) = (1/2)\Delta(R_1 - R_2 + R_3 - R_4)$, c) $S_3(E)$ $\phi_3(E^a) = (1/2)^{1/2}\Delta(R_2 - R_4)$ $\phi_3(E^b) = (1/2)^{1/2}\Delta(R_1 - R_3)$, d) $S_4(A_1)$ $\phi_4(A_1) = \Delta R_5$, e) $S_5(A_1)$ $\phi_5(A_1) = \Delta R_6$, f) $S_6(B_2)$ $\phi_6(B_2) = (1/2)\Delta(\alpha_{12} - \alpha_{23} + \alpha_{34} - \alpha_{41})$, g) $S_7(E)$ $\phi_7(E^a) = (1/2)^{1/2}\Delta(\alpha_{12} - \alpha_{34})$ $\phi_7(E^b) = (1/2)^{1/2}\Delta(\alpha_{23} - \alpha_{41})$, h) $S_8(A_1)$ $\phi_8(A_1) = (1/8)^{1/2}\Delta(\alpha_{15} - \alpha_{16} + \alpha_{25} - \alpha_{26} + \alpha_{35} - \alpha_{36} + \alpha_{45} - \alpha_{46})$, i) $S_9(B_1)$ $\phi_9(B_1) = (1/8)^{1/2}\Delta(\alpha_{15} - \alpha_{16} - \alpha_{25} + \alpha_{26} + \alpha_{35} - \alpha_{36} + \alpha_{45} + \alpha_{46})$, j) $S_{10}(E)$ $\phi_{10}(E^a) = (1/2)\Delta(\alpha_{15} - \alpha_{16} - \alpha_{35} + \alpha_{36})$ $\phi_{10}(E^b) = (1/2)\Delta(\alpha_{25} - \alpha_{26} - \alpha_{45} + \alpha_{46})$, k) $S_{11}(E)$ $\phi_{11}(E^a) = (1/2)\Delta(\alpha_{15} + \alpha_{16} - \alpha_{35} + \alpha_{36})$ $\phi_{11}(E^b) = (1/2)\Delta(\alpha_{25} + \alpha_{26} - \alpha_{45} + \alpha_{46})$; l) atom numbering.

TABLE S-III. Distribution of symmetry vibrations of $[M(NH_3)_5X]^{2+}$ among the irreducible representations of the point group C_{4v} ($\Gamma^{VIB} = 12A_1 + 4A_2 + 7B_1 + 5B_2 + 16E$); ν = stretching, δ = bending (deformation), ρ = rocking, s = symmetric, a = antisymmetric

Motion	A_1	A_2	B_1	B_2	E
Skeletal[a] stretch	S_1: $\nu_s(MN)^{eq}$ S_4: $\nu(MN)^{ax}$ S_5: $\nu(MX)$		S_2: $\nu_{as}(MN)^{eq}$		S_3: $\nu_a(MN)^{eq}$
Skeletal[a] bend	S_8: $\delta(MN_5X)$		S_9: $\delta(NMN)^{eq}$	S_6: $\delta(NMN)^{eq}$	S_7: $\delta(NMN)^{eq}$ S_{10}: $\delta(MN_5X)$ S_{11}: $\delta(MN_5X)$
Sym. stretch	$\nu_s(NH)^{eq}$ $\nu_s(NH)^{ax}$		$\nu_s(NH)^{eq}$		$\nu_s(NH)^{eq}$
As. stretch	$\nu_{as}(NH)^{eq}$	$\nu_{as}(NH)^{eq}$	$\nu_{as}(NH)^{eq}$	$\nu_{as}(NH)^{eq}$	$\nu_{as}(NH)^{eq}$ $\nu_{as}(NH)^{eq}$ $\nu_{as}(NH)^{ax}$
Bend	$\delta_{as}(HNH)^{eq}$	$\delta_{as}(HNH)^{eq}$	$\delta_{as}(HNH)^{eq}$	$\delta_{as}(HNH)^{eq}$	$\delta_{as}(HNH)^{eq}$ $\delta_{as}(HNH)^{eq}$ $\delta_{as}(HNH)^{ax}$
Rock	$\rho_{as}(NH_3)^{eq}$	$\rho_{as}(NH_3)^{eq}$	$\rho_{as}(NH_3)^{eq}$	$\rho_{as}(NH_3)^{eq}$	$\rho_{as}(NH_3)^{eq}$ $\rho_{as}(NH_3)^{eq}$ $\rho_{as}(NH_3)^{ax}$
UMB[b]	$\delta_s(NH_3)^{eq}$ $\delta_s(NH_3)^{ax}$		$\delta_s(NH_3)^{eq}$		$\delta_s(NH_3)^{eq}$
Torsion	$\tau_{as}(NH_3)^{eq}$	$\tau_{as}(NH_3)^{ax}$		$\tau_{as}(NH_3)^{eq}$	$\tau_{as}(NH_3)^{eq}$

[a]S_i = Skeletal symmetry modes depicted in Fig. S-2; [b]UMB = Symmetrical NH_3 bending ≡ umbrella mode

TABLE S-IV. Calculated[a] vibrational frequencies (cm^{-1}) for $[Cr(NH_3)_5X]^{2+}$; ν = stretching, δ = bending (deformation), ρ = rocking, s = symmetric, a = antisymmetric

No.	Principal assignment	X = F			X = Cl			X = Br			X = I		
		Exp.	CFF	DFT	Exp.	CFF	DFT	Exp.	CFF	DFT	Exp.	CFF	DFT
1	$\nu_a(NH_3)$		3277	3388	3277	3275	3383		3277	3382		3277	3395
2	$\nu_a(NH_3)$		3273	3387		3272	3381		3272	3381		3272	3395
3	$\nu_a(NH_3)$		3271	3387		3272	3380		3271	3380		3271	3394
4	$\nu_a(NH_3)$		3271	3385		3271	3380		3271	3379		3271	3391
5	$\nu_a(NH_3)$		3270	3380		3270	3379		3270	3374		3270	3387
6	$\nu_a(NH_3)$		3270	3379		3270	3378		3270	3374		3270	3385
7	$\nu_a(NH_3)$		3269	3367		3270	3367		3270	3365		3270	3373
8	$\nu_a(NH_3)$		3269	3365		3270	3362		3270	3364		3270	3363
9	$\nu_a(NH_3)$		3268	3364		3268	3359		3269	3357		3269	3361
10	$\nu_a(NH_3)$		3267	3363		3268	3357		3268	3355		3269	3358
11	$\nu_s(NH_3)$		3166	3286		3164	3282		3165	3284		3165	3300
12	$\nu_s(NH_3)$		3162	3269		3161	3276		3162	3271		3162	3284
13	$\nu_s(NH_3)$		3160	3266		3160	3271		3161	3270		3161	3277
14	$\nu_s(NH_3)$		3160	3265		3160	3263		3161	3262		3161	3267
15	$\nu_s(NH_3)$		3160	3264		3160	3261		3160	3259		3160	3259
16	δ_a(H–N–H)		1634	1641		1631	1635		1624	1632		1620	1599
17	δ_a(H–N–H)		1627	1627		1618	1625		1613	1629		1611	1593

TABLE S-IV. Continued

No.	Principal assignment	X = F			X = Cl			X = Br			X = I		
		Exp.	CFF	DFT	Exp.	CFF	DFT	Exp.	CFF	DFT	Exp.	CFF	DFT
18	δ_a(H–N–H)		1616	1618		1612	1620		1607	1623		1604	1586
19	δ_a(H–N–H)		1616	1616		1612	1617		1606	1618		1604	1581
20	δ_a(H–N–H)		1590	1614		1589	1608		1587	1607		1586	1574
21	δ_a(H–N–H)		1589	1610		1588	1604		1586	1606		1585	1569
22	δ_a(H–N–H)		1586	1599	1600	1583	1598		1581	1600		1581	1561
23	δ_a(H–N–H)		1583	1599		1580	1589		1580	1585		1579	1555
24	δ_a(H–N–H)		1580	1596		1579	1579		1578	1584		1578	1545
25	δ_a(H–N–H)		1573	1576		1575	1573		1574	1580		1574	1538
26	δ_s(H–N–H)		1366	1354		1336	1356		1372	1356		1338	1341
27	δ_s(H–N–H)		1337	1327		1313	1332		1323	1335		1318	1314
28	δ_s(H–N–H)		1323	1317		1303	1323		1314	1321		1309	1298
29	δ_s(H–N–H)		1312	1315	1289	1293	1314		1300	1306		1297	1292
30	δ_s(H–N–H)		1305	1300		1287	1318		1290	1303		1289	1284
31	$\rho(NH_3)$		804	768	774	758	732		765	727		759	714
32	$\rho(NH_3)$		775	703		742	702		739	698		726	700
33	$\rho(NH_3)$		748	699		712	691		711	696		700	697
34	$\rho(NH_3)$		744	692		702	687		703	692		692	688
35	$\rho(NH_3)$		731	657		694	659		696	663		690	654
36	$\rho(NH_3)$		710	649		686	655		686	651		675	640
37	$\rho(NH_3)$		697	638		679	644		667	637		661	617
38	$\rho(NH_3)$		685	598		662	583		665	573		658	566
39	$\rho(NH_3)$		641	594		628	570		622	569		619	556
40	$\rho(NH_3)$		622	587		613	560		617	558		615	545
41	ν_a(Cr–X)	540	534	554	306	305	344	206	187	179	195	177	176
42	ν_a(Cr–N)	470	474	435		469	433		470	430		471	438
43	ν_a(Cr–N)	462	473	434	472	469	427	470	470	427	467	469	436
44	ν_s(Cr–N)	428	439	411	460	448	425	453	449	413	454	450	415
45	ν_s(Cr–N)	339	387	402	433	407	414	438	403	403	442	402	393
46	ν_a(Cr–N)		380	389	406	371	385	427	372	385	417	370	388
47	$\delta(CrN_5X)$		313	249		296	224		293	276		298	220
48	$\delta(CrN_5X)$		289	236	285	281	218		293	236		288	213
49	$\delta(CrN_5X)$	275	274	224	255	266	215	274	271	216	261	269	179
50	$\delta(CrN_5X)$	260	257	211		241	203	259	263	213	250	257	194
51	$\delta(CrN_5X)$		248	196		226	201	248	244	209	240	244	185
52	$\delta(CrN_5X)$	238	235	188		221	188		225	196		222	183
53	$\delta(CrN_5X)$		223	158	200	200	164		196	188		196	162
54	$\delta(CrN_5X)$	214	217	150		192	153		189	185		184	138
55	$\delta(CrN_5X)$		190	146	170	167	144	171	171	175	168	163	124
56	$\delta(CrN_5X)$	184	181	137		152	136		153	158		149	122
57	$\delta(CrN_5X)$		158	131		143	130		137	137		135	114
58	$\delta(CrN_5X)$		136	118	126	127	81	122	128	128		123	94
59	$\delta(CrN_5X)$	114	120	86	114	103	73	114	117	119	112	111	80
60	$\delta(CrN_5X)$		51	57		43	31		21	56		29	44

[a]Scaling factor for DFT (0.9833)[8]

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