Electronic Supplemental Information.

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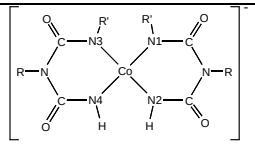
DFT calculations – geometry

DFT is a powerful tool in chemistry, which is able to treat a great variety of chemical species, including open-shell coordination compounds. We have evaluated the effect of basis set on the geometry and excitation energies, and have furthermore examined the relative stability of various possible spin states of $[Co(biur)_2]^-$.

The optimized structures of $[Co(biur)_2]^-$ and $[Co(R,R\text{-bn}(biur)_2)]^-$ are characterized in terms of Co-N distances and N-Co-N angles as shown in **Table S1**.

The Co-N bond lengths and angles obtained by DFT are in excellent agreement with the data available from crystal structure determinations of related compounds. The very short Co-N distances of ca. 1.85 Å illustrates the strong electron donating character of the ligand. There is a clear tendency for increasing bond length with increasing basis set size. In fact, the smallest basis set gives the best agreement with the crystallographic data in the case of the Co-N bond. The bond angles are in fair agreement, in particular for the TZV basis set, and this basis set was found to be the best suited for further calculations. While $[Co(biur)_2]^-$ is completely planar and of D_{2h} symmetry, the bridged compound, $[Co(R,R\text{-bn}(biur)_2)]^-$ was predicted to be slightly skewed with C_2 symmetry. As for $[Co(biur)_2]^-$, $[Co(R,R\text{-bn}(biur)_2)]^-$ were found to have a stable triplet ground state, ^3B. The geometric parameters for $[Co(R,R\text{-bn}(biur)_2)]^-$ at the UB3LYP/TZV level, were in fair agreement with the values from the crystal structure of $[Co(R,S\text{-stien}(biur)_2)]^-$, but with the same trend for slightly shorter Co-N bonds as seen in the non-bridged species. The N-Co-N angles are markedly affected by the presence of the bridge, but this change is well-predicted by the applied DFT method.

Table S1. Comparison of geometric parameters for some Co(III) bisbiuretato compounds.

Level of theory / reference	[a] UB3LYP/ 6-31G*	[a] UB3LYP/ LanL2DZ	[a] UB3LYP/ TZV	[a] UB3LYP/ 6-311+G(d,2p)	[b] Birker, 1974	[a] UB3LYP/TZV	[c] Langkjær, 1985
	R = H R´ = H				R = Ph R´ = H	R = H R´ = CH(Me)-CH(Me) = R´	R = H R´ = CH(Ph)-CH(Ph) = R´
Co-N1 / Å	1.848	1.859	1.860	1.882	1.84(2)	1.866	1.846(3)
Co-N2 / Å					1.83(2)	1.856	1.834(3)
N1-Co-N2 / °	90.37	90.96	90.45	90.16	90.5(9)	92.4	92.1(1)
N1-Co-N3 / °	89.63	89.04	89.55	89.84	89.5(9)	86.1	86.5(1)

[a] DFT calculation, this study, [b] Crystal structure, ref. 4, [c] Crystal structure, ref. 6

DFT calculations – spin state

It is of interest to evaluate how DFT predicts the relative stability of spin states for unusual species, such as $[Co(biur)_2]^-$. It was found that the $^3B_{1g}$ state was the most stable, and vertical energy differences to ^1A_g and ^5A_g were 1.14 μm^{-1} and 1.75 μm^{-1} respectively. For singlet and quintet spin states geometry optimizations within the D_{2h} point group were carried out using the optimized geometry of the triplet as a starting point. The singlet converged with one minor imaginary vibrational frequency (-52.75 cm^{-1}), corresponding to a twisting of the two biuret planes. Attempts to optimize the geometry in a point group of lower symmetry resulted in non-converging wavefunctions, but it is plausible that a more stable singlet state with a more twisted or even D_{2d} symmetry can be attained. In a similar fashion the quintet spin state calculations yielded a converged geometry in D_{2h}, which had a single imaginary frequency (-44.72 cm^{-1}), again corresponding to a twisting of the biuret units. Upon changing the point group to D_{2d} a more stable geometry and electronic state was reached. **Table S2** summarizes the relative energies of the calculations of various spin states and geometries, all obtained using UB3LYP with the TZV basis set.

Table S2: Relative energy of low, intermediate and high spin states of $[Co(biur)_2]^-$ at the UB3LYP/TZV level.

Point group	**D_{2h}**					**D_{2d}**
Electronic state	$^3B_{1g}$	$^1A_{1g}$		$^5A_{1g}$		$^5A_2$
Geometry	Optimized	Vertical	Optimized	Vertical	Optimized	Optimized
Energy / kJ mol^{-1}	0.00	152	136	221	164	87.3
Energy / μm^{-1}	0.00	1.27	1.14	1.85	1.37	0.73

Time-dependent DFT and electronic spectra

The effect of basis set on TD- DFT excitation energies is illustrated by examining the six lowest transitions in $[Co(biur)_2]^-$ as shown in **Table S3**.

Table S3: Effect of basis set for various TD-UB3LYP calculations at different geometries. Transition energies are given in μm^{-1} for the six lowest excited states.

Basis set		Excited state number:					
Geometry	TD-DFT	1	2	3	4	5	6
6-31G* 6D	6-31G* 5D	0.749	0.797	1.38	1.55	2.21	2.32
6-31G* 6D	TZV	0.656	0.712	1.30	1.46	2.11	2.20
6-31G* 6D	6-311++G**	0.654	0.712	1.30	1.47	2.08	2.16
6-311++G**	6-311+G*	0.614	0.670	1.27	1.41	2.02	2.09
TZV	TZV	0.637	0.690	1.28	1.44	2.04	2.14

The data in **Table S3** shows that increasing the basis set leads to lower excitation energies. The results at the TZV level are very close to the 6-311++G** calculations, the latter basis set requiring much longer computational resources. A TD calculation was also performed at the 6-311+G* level on a 6-311++G** geometry, yielding values that confirm the trend for lower excitation energies with a larger basis set, although the values cannot be directly compared due to the difference in geometry.

Finally, a TD-UB3LYP/TZV was performed on a UB3LYP/TZV geometry resulting in excitation energies which are comparable to the values obtained with larger basis sets, but requiring less computational resources. Thus, we find that the TZV basis is a suitable choice for further studies, and it is possible to add a polarization function by requesting the TZVP basis set in the Gaussian software.

DFT results with Pople basis sets

Table S4 contains characterization of the obtained Kohn-Sham molecular orbitals from a UB3LYP/ 6-311+G* calculation on $[Co(biur)_2]$

Table S4. Characterization of Kohn-Sham (KS) β-orbitals and their eigenvalues in $[Co(biur)_2]^-$ at the UB3LYP/ 6-311+G* level (UB3LYP/6-311+G(d, 2p) level geometry). Both α and β orbitals up to number 65 are occupied, while 66α and 67α are the singly occupied KS orbitals. For the most part α and β orbitals are occurring in pairs of similar nature, while there is a difference in the eigenvalues of the α and β KS orbitals. Here results are only shown for β KS orbitals.

β orbital	**type**	**repr.in D_{2h}**	**Explanation**	**E/au**	**E/μm^{-1}**
82	z	b_{1u}	$4p_z$ mix	0.17180	3.770
81	x	b_{3u}	$4p_x$ mix	0.15695	3.445
80	x^2+y^2	a_g	4s mix	0.15600	3.424
79	y	b_{2u}	L sigma	0.15528	3.408
78	yz	b_{3g}	7π	0.15274	3.352
77	z^2	a_g		0.14376	3.155
76	xy	b_{1g}	mainly Lσ	0.14218	3.120
75		a_u	6π	0.13199	2.897
74	zx	b_{2g}	6π	0.12621	2.770
73	z	b_{1u}	7π	0.12371	2.715
72	y	b_{2u}	mainly Lσ	0.12211	2.680
71	y	b_{2u}	mainly Lσ	0.10889	2.390
70	x	b_{3u}	mainly Lσ	0.10881	2.388
69	z^2-x^2	a_g	mainly Lσ	0.07763	1.704
68	xy	b_{1g}	3d mix	0.06700	1.470
67	yz	b_{3g}	3d mix	-0.00346	-0.076
66	zx	b_{2g}	3d mix	-0.00930	-0.204
65		**a_u**	**4π**	**-0.13799**	**-3.028**
64	**x**	**b_{3u}**	**mainly Lσ**	**-0.15240**	**-3.345**
63	**xy**	**b_{1g}**	**mainly Lσ**	**-0.15764**	**-3.460**
62	**z**	**b_{1u}**	**5π**	**-0.16667**	**-3.658**
61	**yz**	**b_{3g}**	**5π**	**-0.16714**	**-3.668**
60	**y**	**b_{2u}**	**mainly Lσ**	**-0.17095**	**-3.752**
59	**zx**	**b_{2g}**	**4π**	**-0.17428**	**-3.825**
58	**z**	**b_{1u}**	**3π**	**-0.17552**	**-3.852**
57	**z^2**	**a_g**	**3d mix**	**-0.17469**	**-3.834**
56	**yz**	**b_{3g}**	**3π**	**-0.17620**	**-3.867**
55	**y^2-z^2**	**a_g**	**3d mix**	**-0.19314**	**-4.239**
54	**x^2**	**a_g**	**3d mix**	**-0.20715**	**-4.546**
53	**x**	**b_{3u}**	**bonding**	**-0.25151**	**-5.520**
52	**y**	**b_{2u}**	**bonding**	**-0.28424**	**-6.238**
51		**a_u**	**2π**	**-0.29094**	**-6.385**
50	**xy**	**b_{1g}**	**bonding**	**-0.29052**	**-6.376**
49	**zx**	**b_{2g}**	**2π**	**-0.29512**	**-6.477**
48	**z^2**	**a_g**	**mainly Lσ**	**-0.32081**	**-7.041**
47	**x**	**b_{3u}**	**mainly Lσ**	**-0.33557**	**-7.365**
46	**y**	**b_{2u}**	**mainly Lσ**	**-0.33583**	**-7.370**
45	**xy**	**b_{1g}**	**mainly Lσ**	**-0.34547**	**-7.582**
44	**yz**	**b_{3g}**	**1π**	**-0.34702**	**-7.616**
43	**z**	**b_{1u}**	**1π**	**-0.34757**	**-7.628**
42		**a_g**	**mainly Lσ**	**-0.35820**	**-7.861**
41	**y**	**b_{2u}**	**mainly Lσ**	**-0.36173**	**-7.939**

Table S5. Characterization of the 20 lowest lying transitions in [Co(biur)2]-.
Level of theory: UB3LYP/ 6-311+G*

Transition	λ / nm	dom. leav.orb	dom. A. orb.	State	f		ΔE/μm^{-1}
0				$^3B_{1g}$			
1	1628	54b ag	66b b2g	$^3B_{3g}$	0	$z^2 \rightarrow zx$	0.614
2	1492	55b ag	67b b3g	$^3B_{2g}$	0	$z^2 \rightarrow yz$	0.670
3	790	54b ag	66b b2g	$^3B_{3g}$	0	$x^2 \rightarrow zx$	1.266
4	709	54b ag	67b b3g	$^3B_{2g}$	0	$x^2 \rightarrow yz$	1.410
5	496	65b au	66b b2g	$^3B_{3u}$	0.0718	4π→zx	2.016
6	478	65b au	67b b3g	$^3B_{2u}$	0.0242	4π→yz	2.092
7	451	56b b3g	66b b2g	^3A_g	0	3π→zx	2.217
8	444	67a b3g	68a b1g	$^3B_{3g}$	0	yz→xy	2.252
9	430	56b b3g	66b b2g	^3A_g	0	3π→zx	2.326
10	426	66a b2g	68a b1g	$^3B_{2g}$	0	zx→xy	2.347
11	415	59b b2g	66b b2g	$^3B_{1g}$	0		2.410
12	415	64b b3u	66b b2g	^3A_u	0		2.410
13	405	54b ag	68b b1g	^3A_g	0		2.469
14	399	59b b2g	67b b3g	^3A_g	0		2.506
15	399	63b b1g	66b b2g	$^3B_{2g}$	0		2.506
16	392	64b b3u	67b b3g	$^3B_{1u}$	0		2.551
17	380	63b b1g	67b b3g	$^3B_{3g}$	0		2.632
18	379	58b b1u	66b b2g	$^3B_{3u}$	0.0152	3π→zx	2.639
19	365	56b b3g	67b b3g	$^3B_{1g}$	0		2.740
20	361	58b b1u	67b b3g	$^3B_{3u}$	0.0395	3π→yz	2.770
21	361	65a au	68a b1g	^3A_u	0.0003	4π→xy	**2.770**
22	357	60b b1g	66b b2g	$^3B_{2g}$	0		2.801
23	355	62b b1u	66b b2g	$^3B_{3u}$	0.014	5π→zx	2.817
24	354	61b b3g	66b b2g	^3A_g	0		2.825
25	341	60b b1g	67b b3g	$^3B_{3g}$	0		2.933
26	339	62b b1u	67b b3g	$^3B_{3u}$	0.0005	5π→yz	2.950
27	339	61b b3g	67b b3g	$^3B_{1g}$	0		2.950
28	322	56a ag	68a b1g	^3A_g	0		3.106
29	320	57b ag	66b b2g	$^3B_{3g}$	0		3.125
30	311	64a b3u	68a b1g	$^3B_{2u}$	0.1631	4π→yz	3.215
31	304	57b ag	67b b3g	$^3B_{2g}$	0		3.289
32	297	59a ag	68a b1g	^3A_g	0		3.367
33	295	63a b1g	68a b1g	$^3B_{1g}$	0		3.390
34	291	58a b1u	68a b1g	$^3B_{1u}$	0		3.436
35	286	62a b2u	68a b1g	$^3B_{2u}$	0.0437	Lσ→yz	3.497
36	284	65b au	68b b1g	^3A_u	0.0005	4π→xy	**3.521**
37	281	60a b3g	68a b1g	$^3B_{3g}$	0		3.559
38	281	61a b1u	68a b1g	$^3B_{1u}$	0		3.559
39	262	56b b3g	68b b1g	$^3B_{3g}$	0		3.817
40	257	59b b2g	68b b1g	$^3B_{2g}$	0		3.891
41	256	59a	68a b1g	$^3B_{1g}$	0		4.840

42	240	64b b3u	68b b1g	$^3B_{3u}$	0.09	σ CT	5.163
43	240	65b au	69b ag	$^3B_{1u}$	0		5.173
44	238	53b	66b b2g	$^3B_{1u}$	0		5.218
45	237	58b b1u	68b b1g	$^3B_{1u}$	0		5.241
46	235	63b b1g	68b b1g	^3A_g	0		5.270
47	234	67a b3g	69a	$^3B_{2g}$	0		5.308
48	231	53b b3u	67b b3g	$^3B_{1u}$	0		5.356
49	229	66a b2g	69a	$^3B_{3g}$	0		5.414
50	227	54a	68a b1g	$^3B_{2g}$	0		5.458
51	227	65a au	69a ag	$^3B_{1u}$	0		5.466
52	226	52a	68a b1g	$^3B_{1g}$	0		5.487
53	224	65a au	72a b3g	$^3B_{2u}$	0.007	6π→7π	**5.525**
54	223	65b au	75b au	$^3B_{1g}$	0		5.559
55	223	62b b1u	68b b1g	$^3B_{1u}$	0		5.563
56	223	61b b3g	68b b1g	$^3B_{3g}$	0		5.564
57	223	60b b1g	68b b1g	$^3B_{2u}$	0.016	σ CT	5.568
58	221	64a b3u	69a ag	$^3B_{2u}$	0.0002	σ CT	5.561
59	219	64b b3u	69b ag	$^3B_{2u}$	0.0193	σ CT	5.654
60	215	63b b1g	69b ag	$^3B_{1g}$	0		5.756
61	215	63b b1g	69b ag	$^3B_{1g}$	0		5.778
62	212	63a	69a	$^3B_{1g}$	0		5.835
63	212	65b au	70b	$^3B_{2g}$	0		5.846
64	212	67a b3g	75a au	$^3B_{2u}$	0.0025	yz→6π	5.858
65	210	64a b3u	72a b3g	$^3B_{1u}$	0		5.899
66	210	63a	72a b3g	$^3B_{2g}$	0		5.911
67	207	62b b1u	69b ag	$^3B_{1u}$	0		5.985
68	207	65b au	71b	$^3B_{3g}$	0		5.986
69	207	57b ag	68b b1g	$^3B_{1g}$	0		6.004
70	206	61b b3g	69b ag	$^3B_{2g}$	0		6.021
71	205	66a b2g	70a	$^3B_{1u}$	0.0001	zx→L CT	6.042
72	205	50b b1g	66b b2g	$^3B_{2g}$	0		6.051
73	204	62a	69a	$^3B_{3u}$	0.0212	σL→σ*	6.075
74	204	55a b1u	68a b1g	$^3B_{1u}$	0.0793	σ CT	6.086
75	204	60a b3g	69a ag	$^3B_{2g}$	0		6.087
76	203	67a b3g	70a b3u	$^3B_{1u}$	0		6.095
77	203	61a b1u	69a ag	$^3B_{1u}$	0.0001	σ CT	6.106
78	202	52b b2u	66b b2g	$^3B_{1u}$	0		6.131
79	202	60b b2u	69b ag	$^3B_{3u}$	0.0691		6.131
80	202	50b b1g	67b b3g	$^3B_{3g}$	0		6.137
81	201	57b ag	69b ag	$^3B_{1g}$	0		6.143
82	201	67a b3g	72a b3g	$^3B_{1g}$	0		6.168
83	201	58b b1u	69b ag	$^3B_{1u}$	0.0105		6.173
84	199	59b b2g	69b ag	$^3B_{3g}$	0		6.222
85	199	56b b3g	69b ag	$^3B_{2g}$	0		6.240
86	199	64b b1g	74b b2g	$^3B_{1u}$	0.0001		6.241

87	199	ag	69a ag	^3A_g	0		6.245
88	198	65a au	70a b3u	$^3B_{2g}$	0		6.254
89	198	67a b3g	71a b2u	$^3B_{1u}$	0.0042	yz→Lσ	6.262
90	197	67a b3g	75a au	$^3B_{2u}$	0.0051	yz→6π	6.303
91	196	64b b3u	76b b1g	$^3B_{2u}$	0		6.310
92	196	59a ag	72a b3g	$^3B_{3g}$	0		6.314
93	196	66a b2g	71a b2u	^3A_u	0		6.325
94	196	62a b2u	72a b3g	^3A_u	0		6.336
95	195	52b b2u	67b b3g	$^3B_{1u}$	0.0002		6.361
96	195	65b au	73b b1u	^3A_g	0		6.361
97	195	65a au	71a b2u	$^3B_{3g}$	0		6.371
98	194	65b au	72b b2u	^3A_u	0		6.384
99	193	64a b3u	71a b2u	$^3B_{1g}$	0		6.408
100	193	64b b3u	70b b3u	^3A_g	0		6.436