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Supplementary Information

Molecular and electronic structure of an azidocobalt(III) complex derived from X-ray crystallography, linear spectroscopy and quantum chemical calculations

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Content:

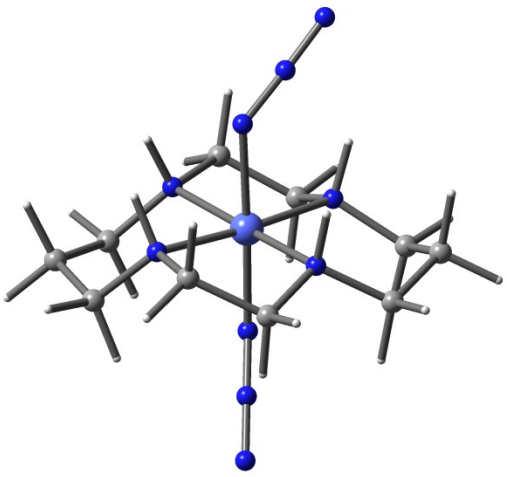
DFT-optimized structures of the five diastereomers.

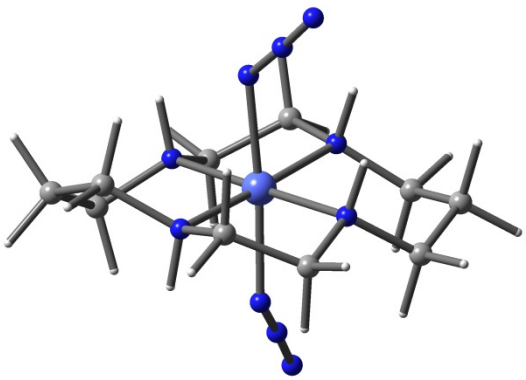
Isomer-I: RSRS, NN-NN improper 132°

N	-0.1015117	-0.1727712	-1.8247213
N	0.7251912	0.2164656	-2.6016139
N	1.4854650	0.5754415	-3.3821447
N	0.2543227	-0.1393732	2.1217474
N	-0.4753100	0.2170019	2.9942908
N	-1.1295558	0.5359723	3.8857241
Co	0.0652706	-0.1183454	0.1604514
N	1.9383955	0.6085102	0.1306481
N	-0.8623114	1.6500529	0.1508771
N	-1.7561676	-0.9436717	0.1003735
N	0.8999856	-1.9454679	0.0591831
H	2.1822820	0.7580833	-0.8481866
H	-0.9090583	1.8492424	-0.8482055
H	-1.7395998	-1.4001726	-0.8090743
H	0.5956694	-2.2941742	-0.8467845
C	2.8053680	-0.4866012	0.6455932
H	2.6629667	-0.5341655	1.7309892
H	3.8650857	-0.2693078	0.4405269
C	2.1851256	1.8957472	0.8323798
H	3.2278706	2.1978169	0.6438979
H	2.0788892	1.7094431	1.9087591
C	1.2363612	3.0021269	0.3863078
H	1.2991148	3.1508472	-0.7052016
H	1.5896795	3.9429542	0.8356009
C	-0.2131437	2.8079513	0.8159472
H	-0.2724014	2.6519957	1.9015582
H	-0.7966661	3.7132113	0.5825665
C	-2.2528957	1.4212540	0.6274608
H	-2.8948596	2.2757616	0.3621069
H	-2.2349356	1.3511259	1.7213109
C	-2.7774591	0.1452577	-0.0036761
H	-2.9718340	0.3082592	-1.0718927
H	-3.7212287	-0.1635095	0.4670537
C	-2.0252066	-1.9964125	1.1148141
H	-1.9575563	-1.5561597	2.1165120
H	-3.0599077	-2.3517495	0.9824326
C	-1.0755031	-3.1829700	0.9482472
H	-1.3482570	-3.9372326	1.7020957
H	-1.2663558	-3.6572369	-0.0310999
C	0.4219766	-2.9090911	1.0868564
H	0.9684925	-3.8569105	0.9552196
H	0.6685075	-2.5048467	2.0756107
C	2.3849325	-1.7836673	-0.0188044
H	2.8909747	-2.6408628	0.4472589
H	2.6632978	-1.7738226	-1.0815944

Isomer-II: RSRS, NN-NN improper -126°

N	0.2361227	0.2067280	-1.6035244
N	0.8316381	-0.5042664	-2.3623699
N	1.3897783	-1.1538437	-3.1268139
N	0.0364239	-0.1922865	2.3375524
N	-0.8731678	-0.2608631	3.1084202
N	-1.7018122	-0.3300825	3.9013505
Co	0.0868713	-0.0603511	0.3601686
N	1.8882613	0.7464934	0.6803270
N	-0.8149061	1.7115431	0.3620814
N	-1.7191938	-0.8373913	-0.0181864
N	1.0141245	-1.8423168	0.3232069
H	1.8958194	0.8540961	1.6944654
H	-0.7985399	1.9840737	-0.6212067
H	-1.6092586	-1.1010201	-0.9941604
H	1.1023541	-2.1129274	-0.6557540
C	2.8959726	-0.2833228	0.3268098
H	3.8757459	-0.0366538	0.7642648
H	3.0124636	-0.2951274	-0.7656851
C	2.1233907	2.0627482	0.0423991
H	1.9533082	1.9247844	-1.0323711
H	3.1797473	2.3450166	0.1756706
C	1.2217817	3.1803989	0.5974861
H	1.0777660	3.9142765	-0.2102114
H	1.7421895	3.7159274	1.4061455
C	-0.1400469	2.7599395	1.1637422
H	-0.0363827	2.3632775	2.1817803
H	-0.7915180	3.6463115	1.2234791
C	-2.2233421	1.4718284	0.7604667
H	-2.8430773	2.3561669	0.5441585
H	-2.2525720	1.3074355	1.8439239
C	-2.7411833	0.2634049	-0.0040053
H	-2.9422445	0.5399577	-1.0474694
H	-3.6825540	-0.0962103	0.4328723
C	-2.0992412	-2.0710918	0.7179195
H	-2.1971575	-1.8360476	1.7850300
H	-3.0911756	-2.3947562	0.3635699
C	-1.0944767	-3.1965357	0.4830262
H	-1.4856816	-4.0989258	0.9773900
H	-1.0561132	-3.4393934	-0.5936225
C	0.3161676	-2.9602660	1.0153779
H	0.9145286	-3.8765953	0.8860765
H	0.2953645	-2.7220223	2.0860565
C	2.3944423	-1.6201276	0.8420157
H	2.3384359	-1.6105775	1.9381456
H	3.0606472	-2.4409061	0.5374030



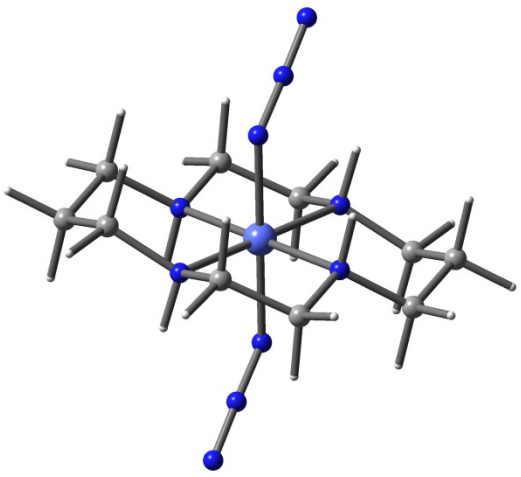


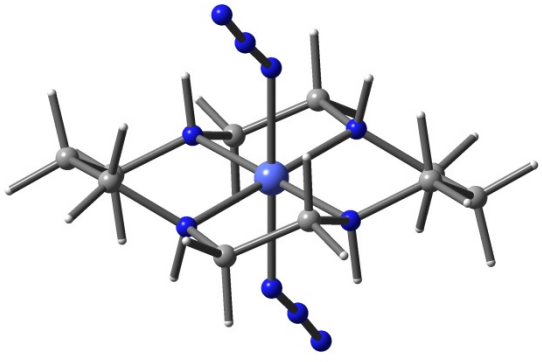
Isomer-III: RSRS, NN-NN improper 180°

N	-0.1550432	0.0593687	-1.9732949
N	0.4673717	-0.6106475	-2.7452476
N	1.0387513	-1.2288146	-3.5277290
N	0.1550516	-0.0593592	1.9732996
N	-0.4673648	0.6106565	2.7452512
N	-1.0387463	1.2288234	3.5277317
Co	0.0000046	0.0000045	0.0000024
N	1.8247939	0.8451782	-0.0033005
N	-0.9748234	1.7663386	0.0240261
N	-1.8247846	-0.8451694	0.0033051
N	0.9748326	-1.7663298	-0.0240214
H	1.9330987	1.0610285	0.9878391
H	-0.9684312	2.0716801	0.9965064
H	-1.9330893	-1.0610198	-0.9878346
H	0.9684401	-2.0716713	-0.9965017
C	2.8171417	-0.2078384	-0.3383735
H	3.8260543	0.0931443	-0.0165997
H	2.8371112	-0.3265285	-1.4305231
C	2.0351200	2.0925129	-0.7766567
H	1.9496164	1.8448392	-1.8433488
H	3.0638984	2.4445208	-0.5966830
C	1.0424539	3.1857115	-0.4031134
H	1.3391188	4.1021306	-0.9358907
H	1.1194825	3.4242322	0.6719577
C	-0.4018548	2.8801110	-0.7768151
H	-1.0270637	3.7737996	-0.6194915
H	-0.4754888	2.5962472	-1.8343403
C	-2.3906701	1.4915959	-0.3414557
H	-2.4371761	1.3864767	-1.4329064
H	-3.0368599	2.3324409	-0.0476263
C	-2.8171325	0.2078472	0.3383779
H	-3.8260451	-0.0931356	0.0166038
H	-2.8371023	0.3265374	1.4305275
C	-2.0351108	-2.0925040	0.7766614
H	-1.9496073	-1.8448302	1.8433534
H	-3.0638891	-2.4445119	0.5966875
C	-1.0424446	-3.1857026	0.4031182
H	-1.3391096	-4.1021216	0.9358956
H	-1.1194732	-3.4242234	-0.6719529
C	0.4018641	-2.8801021	0.7768198
H	1.0270729	-3.7737907	0.6194962
H	0.4754981	-2.5962383	1.8343450
C	2.3906793	-1.4915871	0.3414601
H	2.4371857	-1.3864680	1.4329107
H	3.0368690	-2.3324321	0.0476304

Isomer-IV: RSSR, NN-NN improper 180°

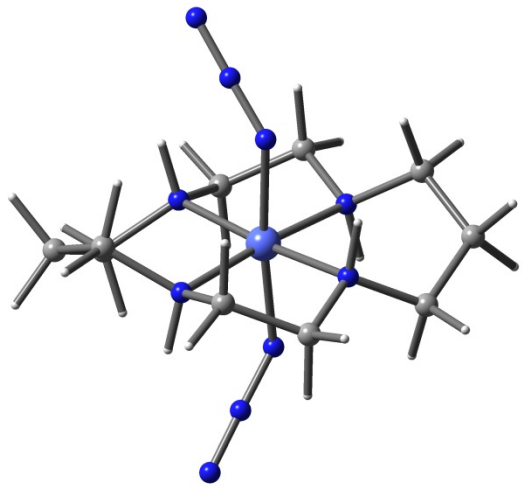
N	0.2705308	-0.1168626	-1.4254805
N	0.9522260	-0.7879509	-2.1430956
N	1.5821979	-1.3949894	-2.8859078
N	-0.1581111	-0.0344779	2.5280974
N	-0.8398209	0.6365955	3.2457124
N	-1.4698054	1.2436172	3.9885277
Co	0.0562075	-0.0756724	0.5513078
N	1.8584931	0.6859770	0.8456640
N	-0.7858905	1.6961727	0.1616433
N	-1.7460780	-0.8373221	0.2569524
N	0.8983064	-1.8475171	0.9409731
H	1.9076566	0.7765258	1.8605715
H	-0.4590284	1.8231709	-0.7932974
H	-1.7952414	-0.9278749	-0.7579546
H	0.5714483	-1.9745110	1.8959159
C	2.8298747	-0.3509418	0.4265514
H	3.8445071	-0.0951289	0.7705829
H	2.8517160	-0.3830929	-0.6684703
C	2.0635250	2.0247803	0.2504281
H	1.8563974	1.9458622	-0.8254652
H	3.1212939	2.3140194	0.3579596
C	1.1989796	3.0915150	0.9267298
H	1.4175554	4.0381496	0.4113727
H	1.5512467	3.2235166	1.9615607
C	-0.3347490	2.8682772	0.9557311
H	-0.6903529	2.7332635	1.9832330
H	-0.8439686	3.7610702	0.5612368
C	-2.2788417	1.5330056	0.0779986
H	-2.5585337	1.5771080	-0.9830009
H	-2.7820167	2.3647297	0.5880684
C	-2.7174602	0.1995983	0.6760599
H	-3.7320917	-0.0562152	0.3320264
H	-2.7393047	0.2317524	1.7710814
C	-1.9511110	-2.1761231	0.8521937
H	-1.7439826	-2.0972012	1.9280865
H	-3.0088802	-2.4653614	0.7446638
C	-1.0865671	-3.2428611	0.1758956
H	-1.3051439	-4.1894938	0.6912557
H	-1.4388348	-3.3748655	-0.8589348
C	0.4471617	-3.0196256	0.1468927
H	0.8027652	-2.8846186	-0.8806103
H	0.9563803	-3.9124170	0.5413919
C	2.3912585	-1.6843511	1.0246104
H	2.6709567	-1.7284583	2.0856082
H	2.8944298	-2.5160735	0.5145342





Isomer-V: RSSR, NN-NN improper -106°

N	-0.0347157	0.1219534	-1.4291276
N	0.4073734	-0.6531491	-2.2259410
N	0.8122037	-1.3727942	-3.0249341
N	0.2563980	0.0232628	2.5292853
N	-0.5944860	-0.2527248	3.3236244
N	-1.3826251	-0.5130688	4.1181658
Co	0.0756755	-0.0223617	0.5496827
N	1.8991774	0.7774055	0.6127692
N	-0.8096195	1.7605553	0.4808819
N	-1.7559817	-0.8115372	0.6671196
N	0.9730071	-1.8051555	0.4428035
H	2.0111082	0.9424335	1.6130069
H	-0.7955567	1.9537771	-0.5203855
H	-1.9392569	-1.0017920	1.6516155
H	0.9912026	-2.0788316	-0.5389926
C	2.8602087	-0.2854082	0.2251918
H	3.8783408	-0.0330308	0.5592411
H	2.8754557	-0.3570007	-0.8714059
C	2.0534749	2.0619872	-0.1068805
H	1.7349960	1.8868085	-1.1422577
H	3.1187328	2.3414615	-0.1321676
C	1.2479591	3.2077361	0.5326922
H	1.0862726	3.9600048	-0.2545044
H	1.8553291	3.7018558	1.3064139
C	-0.0963914	2.8471574	1.1895775
H	0.0487896	2.5112443	2.2240570
H	-0.7339501	3.7449617	1.2205173
C	-2.2264528	1.5642693	0.8778880
H	-2.8467941	2.4108932	0.5461201
H	-2.2778736	1.5210858	1.9750167
C	-2.7050618	0.2595700	0.2568324
H	-2.6906058	0.3221126	-0.8390575
H	-3.7289639	0.0171072	0.5784410
C	-1.9107643	-2.0955371	-0.0601056
H	-2.9745575	-2.3802993	-0.0770939
H	-1.6125188	-1.9150887	-1.0998953
C	-1.0957333	-3.2399165	0.5681733
H	-1.6844264	-3.7214322	1.3639234
H	-0.9641017	-4.0018019	-0.2151876
C	0.2706167	-2.8835150	1.1814709
H	0.9026855	-3.7852640	1.1990743
H	0.1678859	-2.5464392	2.2198105
C	2.3879965	-1.5890291	0.8528902
H	2.4152568	-1.5241298	1.9483587
H	3.0179906	-2.4344358	0.5384940



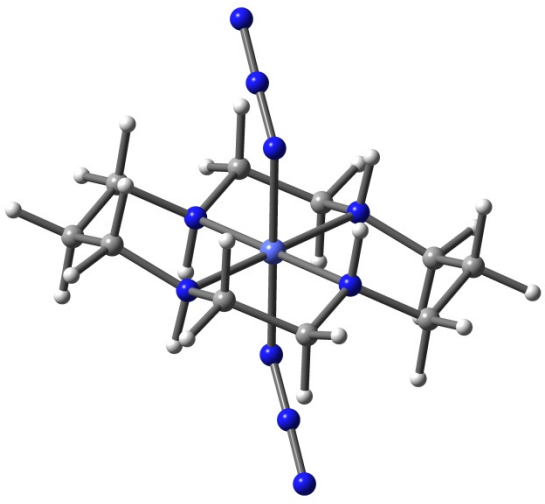
DFT-optimized structures of the eight azide conformer.

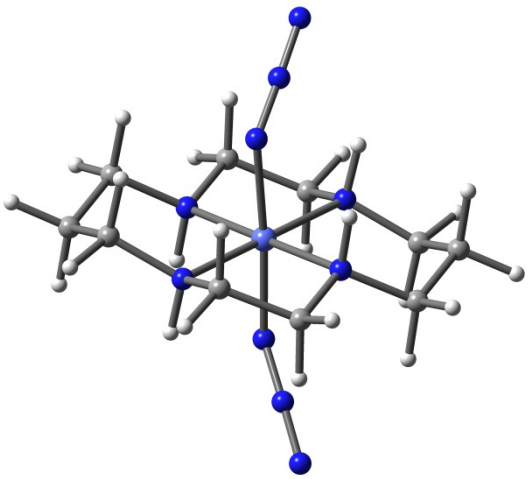
Conformer-1: NN-NN improper 180°

N	-0.2006122	-0.0764449	-1.9637893
N	0.6238574	-0.0819274	-2.8312777
N	1.3629980	-0.0890138	-3.7097043
N	0.2653154	0.1825501	1.9605066
N	-0.5591779	0.1882179	2.8279717
N	-1.2983426	0.1954681	3.7063767
Co	0.0323505	0.0530727	-0.0016406
N	1.8638772	0.8841979	-0.0517991
N	-0.9260635	1.8189862	-0.0199463
N	-1.7991726	-0.7780602	0.0485202
N	0.9907556	-1.7128458	0.0166595
H	1.9575769	1.1151331	0.9378799
H	-0.8788685	2.1220574	0.9521491
H	-1.8928619	-1.0090345	-0.9411505
H	0.9435185	-2.0159237	-0.9554319
C	2.8506058	-0.1830144	-0.3588831
H	3.8598358	0.1191638	-0.0391224
H	2.8765082	-0.3269486	-1.4475539
C	2.0878187	2.1227836	-0.8351325
H	2.0256271	1.8726406	-1.9030239
H	3.1148013	2.4742208	-0.6438231
C	1.0936050	3.2215301	-0.4814224
H	1.3905026	4.1293621	-1.0283125
H	1.1691091	3.4756561	0.5899549
C	-0.3521013	2.9106209	-0.8469073
H	-0.9728634	3.8107979	-0.7093598
H	-0.4327852	2.6071565	-1.8993615
C	-2.3500681	1.5541864	-0.3546257
H	-2.4147952	1.4280653	-1.4430486
H	-2.9813973	2.4087305	-0.0678272
C	-2.7859154	0.2891541	0.3555543
H	-3.7951346	-0.0130354	0.0357710
H	-2.8118487	0.4331098	1.4442217
C	-2.0231091	-2.0166175	0.8319004
H	-1.9609034	-1.7664368	1.8997822
H	-3.0500948	-2.3680583	0.6406154
C	-1.0289036	-3.1153789	0.4782131
H	-1.3257929	-4.0231904	1.0251419
H	-1.1044304	-3.3695435	-0.5931534
C	0.4168110	-2.8044619	0.8436577
H	1.0375686	-3.7046429	0.7061157
H	0.4975179	-2.5009720	1.8961025
C	2.4147738	-1.4480566	0.3512892
H	2.4795421	-1.3219536	1.4397120
H	3.0460885	-2.3025994	0.0644550

Conformer-2: NN-NN improper 135°

N	-0.1977434	-0.0482306	-1.9654824
N	0.6292858	-0.0140306	-2.8294673
N	1.3712597	0.0169984	-3.7052876
N	0.1925695	-0.0212009	1.9735341
N	-0.4408453	0.6346296	2.7492560
N	-1.0207654	1.2390972	3.5357658
Co	0.0216274	0.0268662	0.0028544
N	1.8483475	0.8673964	-0.0068962
N	-0.9520438	1.7899063	0.0227255
N	-1.8046877	-0.8178379	0.0241477
N	0.9891573	-1.7372958	-0.0280928
H	1.9498007	1.0653789	0.9887430
H	-0.9452211	2.0983131	0.9944046
H	-1.9027665	-1.0406525	-0.9668882
H	0.9433885	-2.0099414	-1.0088701
C	2.8403787	-0.1850869	-0.3501780
H	3.8481003	0.1113656	-0.0206836
H	2.8661821	-0.2916808	-1.4430585
C	2.0707505	2.1311960	-0.7515542
H	2.0242772	1.9086955	-1.8262219
H	3.0922611	2.4853012	-0.5376745
C	1.0634003	3.2135223	-0.3850833
H	1.3614087	4.1356828	-0.9068812
H	1.1223373	3.4446692	0.6926434
C	-0.3747056	2.9008522	-0.7780236
H	-1.0039316	3.7938089	-0.6329833
H	-0.4387322	2.6156247	-1.8364656
C	-2.3688733	1.5154021	-0.3402843
H	-2.4157277	1.4017919	-1.4308408
H	-3.0127498	2.3598170	-0.0519163
C	-2.7968287	0.2369673	0.3497595
H	-3.8055671	-0.0657089	0.0288235
H	-2.8186679	0.3647569	1.4409393
C	-2.0107828	-2.0612848	0.8024789
H	-1.9111531	-1.8146947	1.8683372
H	-3.0428938	-2.4103512	0.6355739
C	-1.0261358	-3.1561116	0.4122557
H	-1.3180580	-4.0748049	0.9436236
H	-1.1172511	-3.3869923	-0.6632973
C	0.4238092	-2.8562087	0.7683499
H	1.0443360	-3.7502480	0.5946671
H	0.5123297	-2.5832465	1.8278907
C	2.4109164	-1.4751980	0.3163250
H	2.4745643	-1.3859738	1.4084344
H	3.0480716	-2.3156814	0.0019608



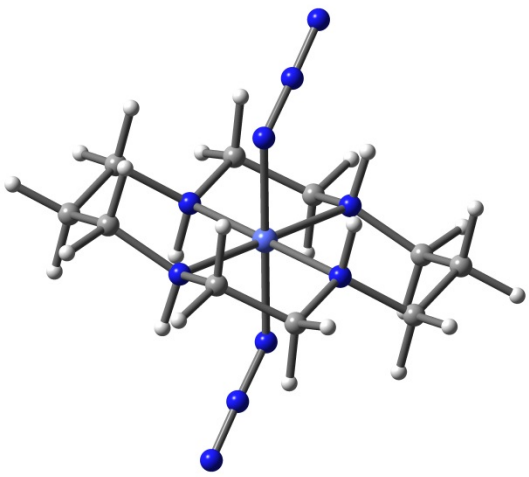


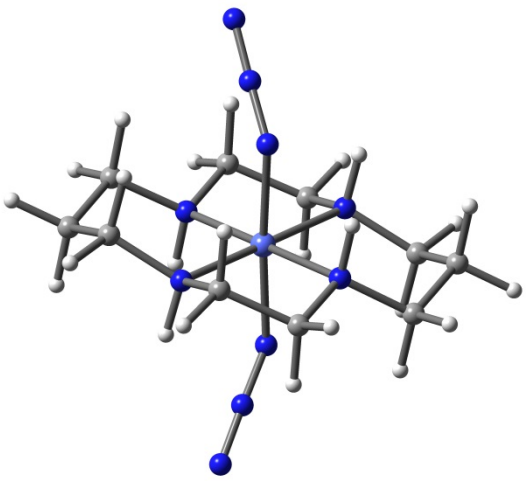
Conformer-3: NN-NN improper 180°

N	-0.1498269	0.0671956	-1.9730446
N	0.4672228	-0.6057293	-2.7467804
N	1.0331710	-1.2267649	-3.5309294
N	0.1841697	-0.0395092	1.9719577
N	-0.4328338	0.6334659	2.7456873
N	-0.9987402	1.2545492	3.5298290
Co	0.0171769	0.0138479	-0.0005437
N	1.8436549	0.8549321	-0.0175410
N	-0.9534288	1.7824824	0.0236547
N	-1.8093016	-0.8272348	0.0164551
N	0.9877840	-1.7547853	-0.0247429
H	1.9581259	1.0736935	0.9722663
H	-0.9404429	2.0909766	0.9950711
H	-1.9237739	-1.0459910	-0.9733533
H	0.9748018	-2.0632749	-0.9961603
C	2.8315958	-0.2014072	-0.3551288
H	3.8431271	0.0983379	-0.0405053
H	2.8446500	-0.3236584	-1.4469830
C	2.0523036	2.0992831	-0.7961486
H	1.9600219	1.8483636	-1.8615202
H	3.0829230	2.4494670	-0.6233084
C	1.0643502	3.1959891	-0.4204280
H	1.3598058	4.1098390	-0.9582697
H	1.1484770	3.4381915	0.6532679
C	-0.3828520	2.8923231	-0.7843247
H	-1.0051394	3.7879148	-0.6262040
H	-0.4634982	2.6051041	-1.8404285
C	-2.3720488	1.5097118	-0.3324560
H	-2.4253272	1.4011577	-1.4232692
H	-3.0146259	2.3529150	-0.0374814
C	-2.7972388	0.2291047	0.3540516
H	-3.8087732	-0.0706389	0.0394365
H	-2.8102835	0.3513558	1.4459062
C	-2.0179492	-2.0715889	0.7950570
H	-1.9256641	-1.8206743	1.8604294
H	-3.0485691	-2.4217717	0.6222172
C	-1.0299967	-3.1682926	0.4193281
H	-1.3254532	-4.0821469	0.9571618
H	-1.1141222	-3.4104854	-0.6543700
C	0.4172050	-2.8646300	0.7832291
H	1.0394922	-3.7602210	0.6251044
H	0.4978492	-2.5774171	1.8393345
C	2.4064019	-1.4820146	0.3313754
H	2.4596742	-1.3734615	1.4221888
H	3.0489808	-2.3252173	0.0364035

Conformer-4: NN-NN improper -135°

N	-0.1625537	0.0479053	-1.9753439
N	0.4677735	-0.6217628	-2.7417650
N	1.0437670	-1.2402867	-3.5201383
N	0.2634229	0.1769113	1.9579784
N	-0.5558949	0.1613903	2.8298200
N	-1.2901475	0.1497230	3.7125669
Co	0.0270009	0.0504662	-0.0056996
N	1.8581939	0.8819209	-0.0642154
N	-0.9287894	1.8213384	-0.0127479
N	-1.8042774	-0.7780977	0.0401670
N	0.9885943	-1.7191337	0.0121357
H	1.9657001	1.1291306	0.9200452
H	-0.8732171	2.1203505	0.9599538
H	-1.9130937	-1.0004950	-0.9495621
H	0.9705766	-2.0525865	-0.9511224
C	2.8405788	-0.1876383	-0.3707087
H	3.8539842	0.1166002	-0.0664091
H	2.8521524	-0.3436972	-1.4583064
C	2.0666968	2.1035514	-0.8757966
H	1.9584168	1.8303201	-1.9343321
H	3.1021890	2.4498271	-0.7248645
C	1.0918708	3.2146236	-0.5075990
H	1.3850185	4.1166730	-1.0661227
H	1.1933024	3.4741011	0.5604137
C	-0.3627585	2.9144468	-0.8438817
H	-0.9761681	3.8169904	-0.6896854
H	-0.4614877	2.6132997	-1.8948483
C	-2.3549252	1.5592874	-0.3389082
H	-2.4280188	1.4425434	-1.4278431
H	-2.9845060	2.4114280	-0.0410420
C	-2.7870014	0.2892263	0.3635267
H	-3.7990444	-0.0091114	0.0492546
H	-2.8039436	0.4233958	1.4535017
C	-2.0299275	-2.0208688	0.8185640
H	-1.9753541	-1.7710117	1.8868139
H	-3.0550361	-2.3735015	0.6201579
C	-1.0320064	-3.1191845	0.4746290
H	-1.3311375	-4.0242965	1.0248744
H	-1.1013472	-3.3806983	-0.5954505
C	0.4110999	-2.8045438	0.8470897
H	1.0337978	-3.7050034	0.7213991
H	0.4855659	-2.4912427	1.8968538
C	2.4103576	-1.4448880	0.3557486
H	2.4674124	-1.3033748	1.4425961
H	3.0462399	-2.3007385	0.0837932



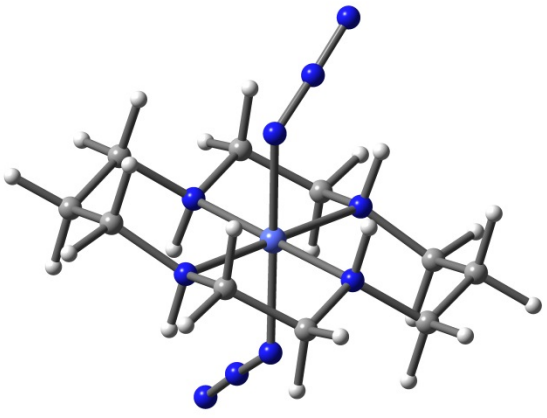


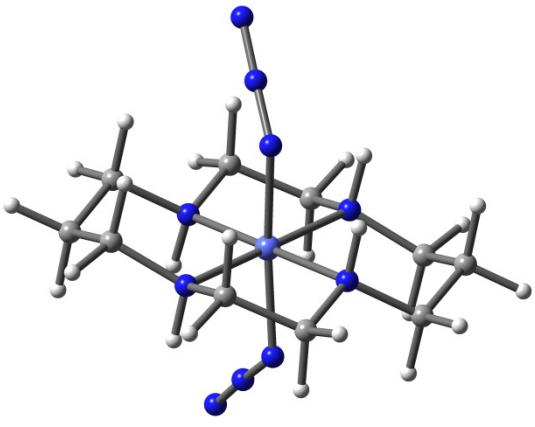
Conformer-5: NN-NN improper 76°

N	0.0826326	-0.0006209	-1.9757801
N	-0.8120549	-0.2988169	-2.7124643
N	-1.6413533	-0.5748292	-3.4591578
N	0.1275044	-0.0624573	1.9774745
N	-0.3790447	0.7114228	2.7368320
N	-0.8467929	1.4284770	3.5040125
Co	-0.0144289	0.0099206	0.0030296
N	1.8175897	0.8467742	-0.0094158
N	-0.9768498	1.7806570	0.0254585
N	-1.8487512	-0.8266148	0.0285865
N	0.9483032	-1.7578403	-0.0332597
H	1.9569478	1.0579311	0.9782466
H	-0.9465213	2.0930072	0.9959162
H	-2.0466232	-1.0778692	-0.9396127
H	0.9021948	-1.9937812	-1.0238495
C	2.7881436	-0.2134984	-0.3824515
H	3.8101189	0.0772179	-0.0945061
H	2.7572455	-0.3251600	-1.4743605
C	2.0238560	2.0900812	-0.7909928
H	1.9279447	1.8291165	-1.8531098
H	3.0548398	2.4403740	-0.6203532
C	1.0372082	3.1909546	-0.4246287
H	1.3354246	4.1004333	-0.9683987
H	1.1165137	3.4422231	0.6473668
C	-0.4098447	2.8874710	-0.7896657
H	-1.0320222	3.7835612	-0.6341452
H	-0.4901983	2.6002521	-1.8460211
C	-2.4053463	1.5167631	-0.2962372
H	-2.4970703	1.4159692	-1.3862391
H	-3.0363263	2.3624421	0.0161905
C	-2.8185702	0.2379220	0.4014207
H	-3.8423244	-0.0540371	0.1222176
H	-2.7910970	0.3589481	1.4927215
C	-2.0333159	-2.0667314	0.8272869
H	-1.8905281	-1.8087354	1.8846720
H	-3.0730870	-2.4081507	0.6993040
C	-1.0693143	-3.1692725	0.4092770
H	-1.3639793	-4.0892828	0.9368916
H	-1.1815106	-3.3895133	-0.6667019
C	0.3892722	-2.8888802	0.7450745
H	0.9992082	-3.7842887	0.5425941
H	0.4968388	-2.6413212	1.8092646
C	2.3710606	-1.4971943	0.3012674
H	2.4456611	-1.4012714	1.3926049
H	3.0043841	-2.3403962	-0.0143602

Conformer-6: NN-NN improper -17°

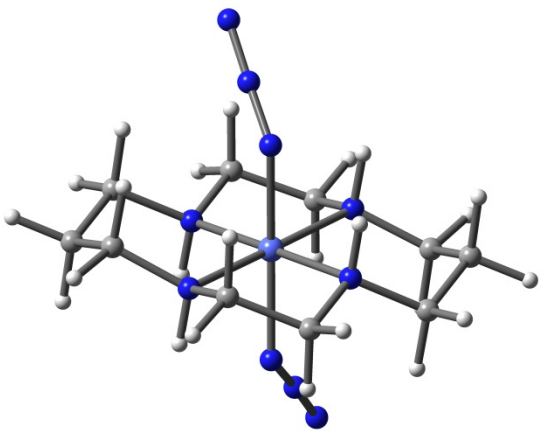
N	0.0792010	-0.0201574	-1.9834445
N	-0.8293555	-0.3092319	-2.7066800
N	-1.6715399	-0.5790267	-3.4410886
N	0.2422783	0.1566224	1.9563313
N	-0.5667185	0.2103377	2.8355873
N	-1.2911275	0.2594145	3.7256941
Co	0.0013169	0.0478923	-0.0067363
N	1.8388499	0.8732550	-0.0661241
N	-0.9461749	1.8203143	-0.0145273
N	-1.8374680	-0.7748007	0.0537387
N	0.9542398	-1.7225069	0.0003128
H	1.9677539	1.1085214	0.9181098
H	-0.8743927	2.1200893	0.9571141
H	-2.0323800	-1.0400032	-0.9112205
H	0.8989378	-1.9879606	-0.9826047
C	2.8007520	-0.2015171	-0.4127711
H	3.8264612	0.0920599	-0.1410632
H	2.7620082	-0.3473494	-1.5005011
C	2.0442399	2.0957580	-0.8763497
H	1.9285138	1.8168043	-1.9321055
H	3.0808886	2.4404359	-0.7293343
C	1.0726841	3.2098756	-0.5095476
H	1.3687949	4.1109085	-1.0682066
H	1.1703220	3.4707614	0.5585051
C	-0.3821074	2.9132092	-0.8480278
H	-0.9944905	3.8161937	-0.6927375
H	-0.4809189	2.6164524	-1.9005270
C	-2.3810199	1.5694342	-0.3109213
H	-2.4881200	1.4609581	-1.3988496
H	-2.9985955	2.4249637	0.0019729
C	-2.8058455	0.3021561	0.4014353
H	-3.8274307	0.0106047	0.1141955
H	-2.7927090	0.4375359	1.4907739
C	-2.0365715	-2.0061081	0.8650237
H	-1.9273933	-1.7416554	1.9249470
H	-3.0733359	-2.3496513	0.7202139
C	-1.0659627	-3.1156739	0.4820001
H	-1.3624005	-4.0217069	1.0321636
H	-1.1718360	-3.3645959	-0.5881211
C	0.3917181	-2.8255148	0.8149527
H	0.9996761	-3.7289267	0.6444214
H	0.4998668	-2.5454243	1.8716215
C	2.3820437	-1.4612626	0.3143312
H	2.4669967	-1.3318422	1.4013787
H	3.0062874	-2.3182885	0.0186609





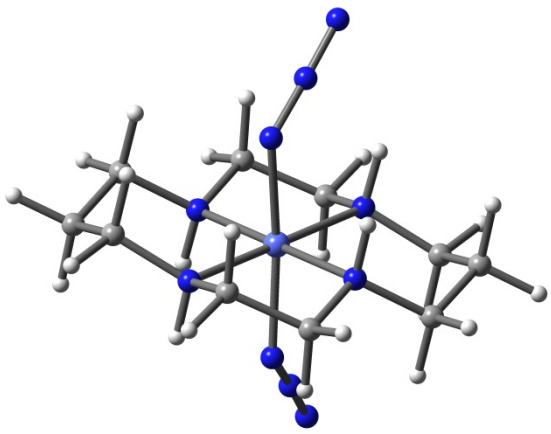
Conformer-7: NN-NN improper 53°

N	0.0297241	-0.1616482	-1.9690283
N	-0.6139490	0.3775825	-2.8212733
N	-1.1955217	0.8589484	-3.6865670
N	0.2498806	0.2002131	1.9575609
N	-0.5551416	0.1718548	2.8423069
N	-1.2748037	0.1494049	3.7368257
Co	-0.0007679	0.0683374	-0.0023218
N	1.8361399	0.8835512	-0.0781897
N	-0.9439335	1.8422812	0.0050954
N	-1.8353423	-0.7490807	0.0574925
N	0.9460337	-1.7069460	0.0082190
H	1.9767114	1.1147611	0.9056812
H	-0.8605999	2.1095735	0.9851155
H	-1.9767152	-0.9943621	-0.9217457
H	0.8666994	-1.9675995	-0.9749905
C	2.7909269	-0.1941516	-0.4365580
H	3.8205463	0.0982292	-0.1790783
H	2.7364133	-0.3428388	-1.5232032
C	2.0342075	2.1116880	-0.8811435
H	1.8963943	1.8469620	-1.9386541
H	3.0768094	2.4465865	-0.7552173
C	1.0829893	3.2304397	-0.4748158
H	1.3811418	4.1400899	-1.0179494
H	1.2040253	3.4645643	0.5968357
C	-0.3825548	2.9643107	-0.7925410
H	-0.9795930	3.8667033	-0.5840327
H	-0.5131975	2.7287300	-1.8568750
C	-2.3840173	1.6034546	-0.2823154
H	-2.5049311	1.5264209	-1.3710723
H	-2.9936814	2.4532309	0.0601896
C	-2.8094572	0.3209522	0.4034343
H	-3.8269952	0.0319218	0.0991786
H	-2.8109701	0.4396660	1.4950550
C	-2.0488632	-1.9900823	0.8481785
H	-1.9637223	-1.7369544	1.9132584
H	-3.0819687	-2.3333375	0.6777029
C	-1.0705656	-3.0978875	0.4793651
H	-1.3729759	-4.0030576	1.0276378
H	-1.1613622	-3.3485909	-0.5915652
C	0.3831401	-2.8040155	0.8278377
H	0.9936018	-3.7077899	0.6674772
H	0.4828164	-2.5190810	1.8842547
C	2.3782300	-1.4510275	0.3006194
H	2.4807576	-1.3187567	1.3860109
H	2.9956860	-2.3105942	-0.0020313



Conformer-7: NN-NN improper -19°

N	0.0611291	-0.1180098	-1.9674574
N	-0.6364285	0.3678041	-2.8087429
N	-1.2645495	0.8067467	-3.6645059
N	0.1367175	-0.0522824	1.9787622
N	-0.3766938	0.7102443	2.7449617
N	-0.8503197	1.4173360	3.5177802
Co	-0.0131199	0.0291038	0.0066875
N	1.8192739	0.8575097	-0.0118191
N	-0.9714821	1.8009489	0.0486824
N	-1.8439851	-0.8011710	0.0249647
N	0.9442998	-1.7439162	-0.0340255
H	1.9658977	1.0625029	0.9762767
H	-0.9343099	2.0886377	1.0262389
H	-1.9968005	-1.0332230	-0.9556692
H	0.8777564	-1.9682501	-1.0267900
C	2.7847587	-0.2037440	-0.3964598
H	3.8091808	0.0844493	-0.1149325
H	2.7447478	-0.3116487	-1.4883561
C	2.0209014	2.1066024	-0.7846002
H	1.9077189	1.8584650	-1.8487388
H	3.0570350	2.4487859	-0.6294930
C	1.0500607	3.2106174	-0.3854690
H	1.3501327	4.1275351	-0.9153346
H	1.1472115	3.4395765	0.6899019
C	-0.4059473	2.9324956	-0.7350796
H	-1.0161451	3.8278214	-0.5351243
H	-0.5130550	2.6987022	-1.8022359
C	-2.4055203	1.5502278	-0.2668026
H	-2.5099912	1.4826473	-1.3576781
H	-3.0287723	2.3896401	0.0761556
C	-2.8196925	0.2552420	0.4003727
H	-3.8396474	-0.0331304	0.1035867
H	-2.8063206	0.3559732	1.4941252
C	-2.0399436	-2.0509335	0.8039557
H	-1.9136442	-1.8048987	1.8666200
H	-3.0780535	-2.3901410	0.6570106
C	-1.0721519	-3.1524509	0.3920801
H	-1.3735932	-4.0735096	0.9139851
H	-1.1731656	-3.3687079	-0.6856874
C	0.3837083	-2.8738082	0.7417841
H	0.9944325	-3.7695354	0.5422896
H	0.4841544	-2.6279128	1.8071712
C	2.3700577	-1.4892840	0.2867677
H	2.4569626	-1.3978517	1.3777269
H	2.9984368	-2.3325457	-0.0387223



CASSCF/NEVPT2/AILFT-results for $[Co(Cyclam)(Cl)_2]^+$

SA-CASSCF(6,5)/def2TZVP(Co,N),def2SVP(C,H) - ab initio ligand field theory
singlet ground-state, root: 5 quintets, 45 triplets, and 50 singlets

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AILFT MATRIX ELEMENTS (CASSCF)
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E0              =  0.007085739 a.u. =     0.193 eV =    1555.1 cm**-1
H(dxy   ,dxy   )= -0.023880894 a.u. =    -0.650 eV =   -5241.3 cm**-1
H(dyz   ,dxy   )= -0.000220210 a.u. =    -0.006 eV =     -48.3 cm**-1
H(dyz   ,dyz   )= -0.020549392 a.u. =    -0.559 eV =   -4510.1 cm**-1
H(dz2   ,dxy   )= -0.001887943 a.u. =    -0.051 eV =    -414.4 cm**-1
H(dz2   ,dyz   )=  0.001393820 a.u. =     0.038 eV =     305.9 cm**-1
H(dz2   ,dz2   )=  0.045036999 a.u. =     1.226 eV =    9884.5 cm**-1
H(dxz   ,dxy   )=  0.000365921 a.u. =     0.010 eV =      80.3 cm**-1
H(dxz   ,dyz   )= -0.000087557 a.u. =    -0.002 eV =     -19.2 cm**-1
H(dxz   ,dz2   )= -0.001795927 a.u. =    -0.049 eV =    -394.2 cm**-1
H(dxz   ,dxz   )= -0.020522573 a.u. =    -0.558 eV =   -4504.2 cm**-1
H(dx2-y2,dxy   )=  0.005025079 a.u. =     0.137 eV =    1102.9 cm**-1
H(dx2-y2,dyz   )=  0.000910251 a.u. =     0.025 eV =     199.8 cm**-1
H(dx2-y2,dz2   )=  0.000083189 a.u. =     0.002 eV =      18.3 cm**-1
H(dx2-y2,dxz   )=  0.000983537 a.u. =     0.027 eV =     215.9 cm**-1
H(dx2-y2,dx2-y2)=  0.062430294 a.u. =     1.699 eV =   13701.9 cm**-1
B               =  0.004956061 a.u. =     0.135 eV =    1087.7 cm**-1
C               =  0.020183648 a.u. =     0.549 eV =    4429.8 cm**-1 (C/B=  4.07)

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0         0.993694   0.062448   0.024094  -0.069179  -0.057496
    2          0.098      792.4        -0.001276  -0.725564  -0.003471  -0.687954   0.016175
    3          0.102      825.8        -0.092012   0.684898  -0.037009  -0.721827   0.006656
    4          1.889    15237.0        -0.027270   0.021366   0.999017  -0.027439   0.003561
    5          2.367    19094.4         0.057969   0.010711  -0.001873   0.012074   0.998186
```

SA-CASSCF-NEVPT2(10,12)/def2TZVP(Co,N),def2SVP(C,H)
singlet ground-state, root: 5 quintet, 20 triplets, and 20 singlets

```
-------------------------------------------------------------------------------------------
                              ABSORPTION SPECTRUM
-------------------------------------------------------------------------------------------
  States           Energy   Wavelength   fosc          T2        TX         TY         TZ
                   (cm-1)     (nm)                   (D**2)      (D)        (D)        (D)
-------------------------------------------------------------------------------------------
  0( 2)-> 1( 2) 1   15761.5    634.5   0.000000000   0.00000   0.00000  -0.00000   0.00000
  0( 2)-> 2( 2) 1   16058.3    622.7   0.000000000   0.00000   0.00000   0.00000  -0.00000
  0( 2)-> 3( 2) 1   20011.6    499.7   0.000000000   0.00000   0.00000   0.00000   0.00000
  0( 2)-> 4( 2) 1   24638.0    405.9   0.000000000   0.00000  -0.00000   0.00000  -0.00000
  0( 2)-> 5( 2) 1   26219.2    381.4   0.000000000   0.00000   0.00000   0.00000   0.00000
  0( 2)-> 6( 2) 1   26945.4    371.1   0.000000000   0.00000   0.00000  -0.00000  -0.00000
  0( 2)-> 7( 2) 1   34956.1    286.1   0.000000000   0.00000   0.00000   0.00000   0.00000
  0( 2)-> 8( 2) 1   35384.9    282.6   0.000000000   0.00000  -0.00000   0.00000  -0.00000
  0( 2)-> 9( 2) 1   38225.0    261.6   0.000000000   0.00000   0.00000  -0.00000  -0.00000
  0( 2)->10( 2) 1   38783.7    257.8   0.000000000   0.00000   0.00000  -0.00000   0.00000
  0( 2)->11( 2) 1   38828.4    257.5   0.000000000   0.00000   0.00000   0.00000   0.00000
  0( 2)->15( 2) 1   42829.6    233.5   0.000000000   0.00000  -0.00000   0.00000  -0.00000
  0( 2)->12( 2) 1   43227.1    231.3   0.000000000   0.00000  -0.00000  -0.00000   0.00000
  0( 2)->13( 2) 1   43259.5    231.2   0.000000000   0.00000  -0.00000  -0.00000  -0.00000
  0( 2)->14( 2) 1   43699.2    228.8   0.000000000   0.00000  -0.00000   0.00000   0.00000
  0( 2)->16( 2) 1   43825.7    228.2   0.000000000   0.00000  -0.00000  -0.00000  -0.00000
  0( 2)->17( 2) 1   44473.5    224.9   0.000000000   0.00000   0.00000   0.00000   0.00000
  0( 2)->18( 2) 1   46130.1    216.8   0.000000000   0.00000  -0.00000   0.00000   0.00000
  0( 2)->19( 2) 1   46161.6    216.6   0.000000000   0.00000   0.00000   0.00000   0.00000
```

NEVPT2 TRANSITION ENERGIES

LOWEST ROOT (ROOT 0, MULT 1) = -2913.775890902 Eh -79287.873 eV 1A1g

STATE	ROOT	MULT	DE/a.u.	DE/eV	DE/cm**-1	SYMMETRY
1:	0	3	0.031845	0.867	6989.1	3Eg(1)
2:	1	3	0.033653	0.916	7386.0	3Eg(1)
3:	2	3	0.050098	1.363	10995.2	3A2g
4:	3	3	0.052717	1.434	11569.9	3B2g
5:	4	3	0.058846	1.601	12915.2	3Eg(2)
6:	0	5	0.060201	1.638	13212.5	5B2g
7:	5	3	0.061538	1.675	13506.1	3Eg(2)
8:	1	5	0.064898	1.766	14243.4	5Eg
9:	2	5	0.065301	1.777	14332.0	5Eg
10:	1	1	0.071815	1.954	15761.5	1Eg(1)
11:	2	1	0.073167	1.991	16058.3	1Eg(1)
12:	3	1	0.091180	2.481	20011.6	1A2g
13:	6	3	0.098119	2.670	21534.7	
14:	4	1	0.112259	3.055	24638.0	1B2g
15:	7	3	0.118935	3.236	26103.2	
16:	5	1	0.119463	3.251	26219.2	1Eg(2)
17:	8	3	0.122407	3.331	26865.3	
18:	9	3	0.122625	3.337	26913.2	
19:	6	1	0.122772	3.341	26945.4	1Eg(2)
20:	10	3	0.129663	3.528	28457.8	
21:	11	3	0.130013	3.538	28534.5	
22:	3	5	0.145084	3.948	31842.4	5A1g
23:	15	3	0.154725	4.210	33958.2	
24:	13	3	0.156587	4.261	34366.9	
25:	12	3	0.158229	4.306	34727.3	
26:	7	1	0.159272	4.334	34956.1	
27:	8	1	0.161225	4.387	35384.9	
28:	14	3	0.161315	4.390	35404.6	
29:	4	5	0.161588	4.397	35464.4	5B1g
30:	16	3	0.165895	4.514	36409.7	
31:	17	3	0.167272	4.552	36711.9	
32:	18	3	0.168128	4.575	36899.8	
33:	19	3	0.172960	4.706	37960.3	
34:	9	1	0.174166	4.739	38225.0	
35:	10	1	0.176711	4.809	38783.7	
36:	11	1	0.176915	4.814	38828.4	
37:	15	1	0.195146	5.310	42829.6	
38:	12	1	0.196957	5.359	43227.1	
39:	13	1	0.197105	5.363	43259.5	
40:	14	1	0.199108	5.418	43699.2	
41:	16	1	0.199685	5.434	43825.7	
42:	17	1	0.202636	5.514	44473.5	
43:	18	1	0.210184	5.719	46130.1	
44:	19	1	0.210328	5.723	46161.6	

ORBITAL ORDERING

```
Orbital number (ORCA): 81 | 82| 83  |   84    |   85    |  86  |  87   | .....
Orbital designation  :  L | L | dxy | dxz/dyz | dxz/dyz |  dz2 | dx2y2 | 2nd d-shell
Ground-state occ     :  2 | 2 |  2  |    2    |    2    |   2  |   2   | 00000
Orbital symmetries   :  - | - | b2g |    eg   |    eg   |  a1g |  b1g  | -----
```

CAS-SCF STATES FOR BLOCK 1 MULT= 5 NROOTS=5

```
ROOT   0:  E=   -2910.6828511444 Eh
      0.95265 [     0]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (a1g)1 (b1g)1   --->   B2g
ROOT   1:  E=   -2910.6791341350 Eh  0.101 eV    815.8 cm**-1
      0.94870 [   126]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (a1g)1 (b1g)1   --->   Eg
ROOT   2:  E=   -2910.6789904469 Eh  0.105 eV    847.3 cm**-1
      0.94943 [   182]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (a1g)1 (b1g)1   --->   Eg
ROOT   3:  E=   -2910.5977256764 Eh  2.316 eV  18682.9 cm**-1
      0.96922 [   203]: 22 1 11 2 1 00000    (b2g)1 (eg)2 (a1g)2 (b1g)1   --->   A1g
ROOT   4:  E=   -2910.5825227859 Eh  2.730 eV  22019.5 cm**-1
      0.96876 [   209]: 22 1 11 1 2 00000    (b2g)1 (eg)2 (a1g)1 (b1g)2   --->   B1g
```

CAS-SCF STATES FOR BLOCK 2 MULT= 3 NROOTS=20

```
ROOT   0:  E=   -2910.6950191057 Eh
      0.77845 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
      0.09173 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
ROOT   1:  E=   -2910.6935525913 Eh  0.040 eV    321.9 cm**-1
      0.74888 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
      0.12266 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
ROOT   2:  E=   -2910.6815007457 Eh  0.368 eV   2966.9 cm**-1
      0.84871 [   379]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (a1g)0 (b1g)1   --->   A2g
ROOT   3:  E=   -2910.6717415531 Eh  0.633 eV   5108.8 cm**-1
      0.79145 [   378]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (a1g)1 (b1g)0   --->   B2g
ROOT   4:  E=   -2910.6684581428 Eh  0.723 eV   5829.5 cm**-1
      0.67052 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
      0.10547 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
ROOT   5:  E=   -2910.6659117750 Eh  0.792 eV   6388.3 cm**-1
      0.70125 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
```

CAS-SCF STATES FOR BLOCK 3 MULT= 1 NROOTS=20

```
ROOT   0:  E=   -2910.7245878023 Eh
      0.87524 [     0]: 22 2 22 0 0 00000    (b2g)2 (eg)4 (a1g)0 (b1g)0   --->   A1g
ROOT   1:  E=   -2910.6533302812 Eh  1.939 eV  15639.2 cm**-1
      0.77217 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
      0.14513 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
ROOT   2:  E=   -2910.6522353697 Eh  1.969 eV  15879.5 cm**-1
      0.76637 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
      0.15532 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
ROOT   3:  E=   -2910.6372923624 Eh  2.375 eV  19159.1 cm**-1
      0.90617 [   415]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (a1g)0 (b1g)1   --->   A2g
ROOT   4:  E=   -2910.6054531856 Eh  3.242 eV  26147.0 cm**-1
      0.73406 [   414]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (a1g)1 (b1g)0   --->   B2g
      0.16984 [    44]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (a1g)1 (b1g)1   --->   B2g
ROOT   5:  E=   -2910.5997155785 Eh  3.398 eV  27406.3 cm**-1
      0.60677 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
      0.18107 [   422]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (a1g)1 (b1g)1   --->   Eg
      0.11478 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
ROOT   6:  E=   -2910.5963280073 Eh  3.490 eV  28149.8 cm**-1
      0.60919 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (a1g)0 (b1g)1   --->   Eg
      0.19283 [   527]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (a1g)1 (b1g)1   --->   Eg
      0.10498 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (a1g)1 (b1g)0   --->   Eg
```

CASSCF/NEVPT2/AILFT-results for $[Co(Cyclam)(N_3)_2]^+$, conformer 3 (180° NN-NN improper dihedral)

SA-CASSCF(6,5)/def2TZVP(Co,N),def2SVP(C,H) - ab initio ligand field theory
singlet ground-state, root: 5 quintets, 45 triplets, and 50 singlets

```
------------------------------
AILFT MATRIX ELEMENTS (CASSCF)
------------------------------

E0                =  0.008146739 a.u. =     0.222 eV =    1788.0 cm**-1
H(dxy   ,dxy   )= -0.027423999 a.u. =    -0.746 eV =   -6018.9 cm**-1
H(dyz   ,dxy   )=  0.000075827 a.u. =     0.002 eV =      16.6 cm**-1
H(dyz   ,dyz   )= -0.019515658 a.u. =    -0.531 eV =   -4283.2 cm**-1
H(dz2   ,dxy   )=  0.001519332 a.u. =     0.041 eV =     333.5 cm**-1
H(dz2   ,dyz   )=  0.008967180 a.u. =     0.244 eV =    1968.1 cm**-1
H(dz2   ,dz2   )=  0.057249282 a.u. =     1.558 eV =   12564.8 cm**-1
H(dxz   ,dxy   )=  0.000340543 a.u. =     0.009 eV =      74.7 cm**-1
H(dxz   ,dyz   )=  0.001915005 a.u. =     0.052 eV =     420.3 cm**-1
H(dxz   ,dz2   )= -0.005352528 a.u. =    -0.146 eV =   -1174.7 cm**-1
H(dxz   ,dxz   )= -0.015527464 a.u. =    -0.423 eV =   -3407.9 cm**-1
H(dx2-y2,dxy   )=  0.005121013 a.u. =     0.139 eV =    1123.9 cm**-1
H(dx2-y2,dyz   )=  0.004369327 a.u. =     0.119 eV =     959.0 cm**-1
H(dx2-y2,dz2   )= -0.001443991 a.u. =    -0.039 eV =    -316.9 cm**-1
H(dx2-y2,dxz   )=  0.001649849 a.u. =     0.045 eV =     362.1 cm**-1
H(dx2-y2,dx2-y2)=  0.054098275 a.u. =     1.472 eV =   11873.2 cm**-1
B                 =  0.005012596 a.u. =     0.136 eV =    1100.1 cm**-1
C                 =  0.019953433 a.u. =     0.543 eV =    4379.3 cm**-1 (C/B=  3.98)

The ligand field one electron eigenfunctions:
Orbital    Energy (eV)  Energy(cm-1)      dxy        dyz        dz2        dxz        dx2-y2
    1          0.000        0.0         0.994444   0.065541  -0.028384  -0.041374  -0.065335
    2          0.165     1327.3        -0.082186   0.913470  -0.128249  -0.375047  -0.041348
    3          0.350     2826.9        -0.010831  -0.380732  -0.020003  -0.923233   0.046549
    4          2.240    18067.6        -0.064792  -0.083947  -0.217834  -0.008817  -0.970168
    5          2.359    19027.5         0.003471   0.096297   0.966900  -0.072047  -0.225009
```

SA-CASSCF-NEVPT2(10,12)/def2TZVP(Co,N),def2SVP(C,H)
singlet ground-state, root: 5 quintet, 20 triplets, and 20 singlets

ABSORPTION SPECTRUM

States	Energy (cm-1)	Wavelength (nm)	fosc	T2 (D**2)	TX (D)	TY (D)	TZ (D)
0(2)-> 1(2) 1	17125.6	583.9	0.000000000	0.00000	0.00000	-0.00000	-0.00000
0(2)-> 2(2) 1	17867.7	559.7	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)-> 3(2) 1	19223.6	520.2	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)-> 4(2) 1	25212.2	396.6	0.000000000	0.00000	0.00000	0.00000	-0.00000
0(2)-> 5(2) 1	26222.2	381.4	0.000000000	0.00000	-0.00000	0.00000	0.00000
0(2)-> 6(2) 1	27792.1	359.8	0.000000000	0.00000	0.00000	-0.00000	-0.00000
0(2)->10(2) 1	38482.0	259.9	0.000000000	0.00000	-0.00000	0.00000	0.00000
0(2)->11(2) 1	38525.6	259.6	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)-> 7(2) 1	38921.3	256.9	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)-> 8(2) 1	39225.0	254.9	0.000000000	0.00000	-0.00000	-0.00000	-0.00000
0(2)-> 9(2) 1	39615.7	252.4	0.000000000	0.00000	-0.00000	-0.00000	0.00000
0(2)->12(2) 1	42324.4	236.3	0.000000000	0.00000	-0.00000	0.00000	0.00000
0(2)->13(2) 1	43132.4	231.8	0.000000000	0.00000	-0.00000	-0.00000	-0.00000
0(2)->14(2) 1	43165.6	231.7	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)->17(2) 1	45146.7	221.5	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)->18(2) 1	45342.9	220.5	0.000000000	0.00000	0.00000	0.00000	-0.00000
0(2)->15(2) 1	45523.8	219.7	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)->19(2) 1	45743.7	218.6	0.000000000	0.00000	0.00000	0.00000	0.00000
0(2)->16(2) 1	46028.6	217.3	0.000000000	0.00000	-0.00000	-0.00000	0.00000

NEVPT2 TRANSITION ENERGIES

LOWEST ROOT (ROOT 0, MULT 1) = -2322.177429540 Eh -63189.660 eV 1A1g

STATE	ROOT	MULT	DE/a.u.	DE/eV	DE/cm**-1	SYMMETRY
1:	2	3	0.041108	1.119	9022.1	3Eg(1)
2:	0	3	0.041748	1.136	9162.6	3Eg(1)
3:	1	3	0.043205	1.176	9482.5	3A2g
4:	3	3	0.053343	1.452	11707.5	3Eg(2)
5:	4	3	0.056380	1.534	12374.0	3Eg(2)
6:	0	5	0.060088	1.635	13187.9	5B2g
7:	5	3	0.068132	1.854	14953.2	3B2g
8:	1	5	0.068207	1.856	14969.8	5Eg
9:	2	5	0.072099	1.962	15823.9	5Eg
10:	1	1	0.078030	2.123	17125.6	1Eg(1)
11:	2	1	0.081411	2.215	17867.7	1Eg(1)
12:	3	1	0.087589	2.383	19223.6	1A2g
13:	4	1	0.114875	3.126	25212.2	1Eg(2)
14:	5	1	0.119477	3.251	26222.2	1Eg(2)
15:	9	3	0.119604	3.255	26250.1	
16:	6	3	0.121388	3.303	26641.5	
17:	7	3	0.121676	3.311	26704.8	
18:	8	3	0.121927	3.318	26759.9	
19:	6	1	0.126630	3.446	27792.1	1B2g
20:	10	3	0.134824	3.669	29590.5	
21:	11	3	0.137985	3.755	30284.2	
22:	3	5	0.157075	4.274	34474.0	5B1g
23:	15	3	0.159465	4.339	34998.6	
24:	14	3	0.159985	4.353	35112.7	
25:	4	5	0.160255	4.361	35171.8	5A1g
26:	12	3	0.160949	4.380	35324.2	
27:	16	3	0.164212	4.468	36040.3	
28:	13	3	0.164758	4.483	36160.2	
29:	17	3	0.170452	4.638	37410.0	
30:	18	3	0.173938	4.733	38174.9	
31:	10	1	0.175337	4.771	38482.0	
32:	11	1	0.175535	4.777	38525.6	
33:	7	1	0.177338	4.826	38921.3	
34:	8	1	0.178722	4.863	39225.0	
35:	19	3	0.178759	4.864	39233.0	
36:	9	1	0.180503	4.912	39615.7	
37:	12	1	0.192844	5.248	42324.4	
38:	13	1	0.196526	5.348	43132.4	
39:	14	1	0.196677	5.352	43165.6	
40:	17	1	0.205703	5.597	45146.7	
41:	18	1	0.206597	5.622	45342.9	
42:	15	1	0.207422	5.644	45523.8	
43:	19	1	0.208424	5.671	45743.7	
44:	16	1	0.209722	5.707	46028.6	

ORBITAL ORDERING

```
Orbital number (ORCA): 85 | 86| 87  |   88    |   89    |   90   | 91  | .....
Orbital designation  :  L | L | dxy | dxz/dyz | dxz/dyz | dx2-y2 | dz2 | 2nd d-shell
Ground-state occ     :  2 | 2 |  2  |    2    |    2    |    2   |  2  | 00000
Orbital symmetries   :  - | - | b2g |    eg   |    eg   |   b1g  | a1g | -----
```

CAS-SCF STATES FOR BLOCK 1 MULT= 5 NROOTS= 5

```
ROOT   0:  E=   -2318.2386451866 Eh
      0.76080 [     0]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (b1g)1 (a1g)1   --->   B2g
      0.18849 [   126]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   1:  E=   -2318.2303817218 Eh  0.225 eV   1813.6 cm**-1
      0.68431 [   126]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
      0.14199 [     0]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (b1g)1 (a1g)1   --->   B2g
      0.12078 [   182]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   2:  E=   -2318.2274900253 Eh  0.304 eV   2448.3 cm**-1
      0.81989 [   182]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   3:  E=   -2318.1435877786 Eh  2.587 eV  20862.7 cm**-1
      0.96778 [   203]: 22 1 11 2 1 00000    (b2g)1 (eg)2 (b1g)2 (a1g)1   --->   B1g
ROOT   4:  E=   -2318.1337976532 Eh  2.853 eV  23011.4 cm**-1
      0.96298 [   209]: 22 1 11 1 2 00000    (b2g)1 (eg)2 (b1g)1 (a1g)2   --->   A1g
```

CAS-SCF STATES FOR BLOCK 2 MULT= 3 NROOTS=20

```
ROOT   0:  E=   -2318.2463058440 Eh
      0.38960 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.32975 [   378]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
      0.11437 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
ROOT   1:  E=   -2318.2450869129 Eh  0.033 eV    267.5 cm**-1
      0.41777 [   378]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
      0.17288 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   2:  E=   -2318.2445538677 Eh  0.064 eV    513.0 cm**-1
      0.40213 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.36176 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   3:  E=   -2318.2443049202 Eh  0.054 eV    439.2 cm**-1
      0.22154 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.19936 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.18056 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.13154 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   4:  E=   -2318.2252654303 Eh  0.573 eV   4617.8 cm**-1
      0.37992 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.18058 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.12527 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   5:  E=   -2318.2099902015 Eh  0.988 eV   7970.4 cm**-1
      0.67520 [   379]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (b1g)0 (a1g)1   --->   B2g
```

CAS-SCF STATES FOR BLOCK 3 MULT= 1 NROOTS=20

```
ROOT   0:  E=   -2318.2820023678 Eh
      0.88132 [     0]: 22 2 22 0 0 00000    (b2g)2 (eg)4 (b1g)2 (a1g)0   --->   A1g
ROOT   1:  E=   -2318.2031198857 Eh  2.147 eV  17312.7 cm**-1
      0.63916 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.19374 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   2:  E=   -2318.2011236564 Eh  2.201 eV  17750.8 cm**-1
      0.44470 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.30633 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   3:  E=   -2318.1991021247 Eh  2.256 eV  18194.5 cm**-1
      0.75039 [   414]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
      0.13102 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   4:  E=   -2318.1597863776 Eh  3.326 eV  26823.3 cm**-1
      0.48375 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.22203 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
ROOT   5:  E=   -2318.1555041518 Eh  3.442 eV  27763.1 cm**-1
      0.42769 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.20817 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.11574 [   527]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   6:  E=   -2318.1474866031 Eh  3.660 eV  29522.8 cm**-1
      0.57119 [   415]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (b1g)0 (a1g)1   --->   B2g
      0.19821 [    44]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (b1g)1 (a1g)1   --->   A1g
```

CASSCF/NEVPT2-results for $[Co(Cyclam)(N_3)_2]^+$, conformer 5 (76° NN-NN improper dihedral)

SA-CASSCF(6,5)/def2TZVP(Co,N),def2SVP(C,H) - ab initio ligand field theory
singlet ground-state, root: 5 quintets, 45 triplets, and 50 singlets

```
------------------------------
AILFT MATRIX ELEMENTS (CASSCF)
------------------------------

E0              =  0.008127829 a.u. =     0.221 eV =    1783.9 cm**-1
H(dxy   ,dxy   )= -0.027360490 a.u. =    -0.745 eV =   -6004.9 cm**-1
H(dyz   ,dxy   )=  0.000008310 a.u. =     0.000 eV =       1.8 cm**-1
H(dyz   ,dyz   )= -0.018065361 a.u. =    -0.492 eV =   -3964.9 cm**-1
H(dz2   ,dxy   )=  0.001888355 a.u. =     0.051 eV =     414.4 cm**-1
H(dz2   ,dyz   )=  0.003157707 a.u. =     0.086 eV =     693.0 cm**-1
H(dz2   ,dz2   )=  0.058278684 a.u. =     1.586 eV =   12790.7 cm**-1
H(dxz   ,dxy   )= -0.000121176 a.u. =    -0.003 eV =     -26.6 cm**-1
H(dxz   ,dyz   )=  0.001368885 a.u. =     0.037 eV =     300.4 cm**-1
H(dxz   ,dz2   )=  0.002961423 a.u. =     0.081 eV =     650.0 cm**-1
H(dxz   ,dxz   )= -0.018193861 a.u. =    -0.495 eV =   -3993.1 cm**-1
H(dx2-y2,dxy   )=  0.005451376 a.u. =     0.148 eV =    1196.4 cm**-1
H(dx2-y2,dyz   )=  0.001532081 a.u. =     0.042 eV =     336.3 cm**-1
H(dx2-y2,dz2   )= -0.000147343 a.u. =    -0.004 eV =     -32.3 cm**-1
H(dx2-y2,dxz   )= -0.001172895 a.u. =    -0.032 eV =    -257.4 cm**-1
H(dx2-y2,dx2-y2)=  0.054107998 a.u. =     1.472 eV =   11875.3 cm**-1
B               =  0.005011513 a.u. =     0.136 eV =    1099.9 cm**-1
C               =  0.019935954 a.u. =     0.542 eV =    4375.4 cm**-1 (C/B=  3.98)
```

The ligand field one electron eigenfunctions:

Orbital	Energy (eV)	Energy(cm-1)	dxy	dyz	dz2	dxz	dx2-y2
1	0.000	0.0	0.997348	0.015805	-0.022901	0.009286	-0.066607
2	0.224	1804.0	-0.005976	0.692587	-0.000574	-0.720860	-0.025444
3	0.293	2362.3	-0.019334	0.719649	-0.056915	0.691725	-0.002731
4	2.239	18060.7	-0.066447	-0.020793	-0.000683	0.015780	-0.997448
5	2.349	18948.9	0.021732	0.041783	0.998116	0.039253	-0.002381

SA-CASSCF-NEVPT2(10,12)/def2TZVP(Co,N),def2SVP(C,H)
singlet ground-state, root: 5 quintet, 20 triplets, and 20 singlets

ABSORPTION SPECTRUM

States	Energy (cm-1)	Wavelength (nm)	fosc	T2 (D**2)	TX (D)	TY (D)	TZ (D)
0(2)-> 1(2) 1	17282.8	578.6	0.000004003	0.00049	0.01569	-0.01551	0.00225
0(2)-> 2(2) 1	17734.1	563.9	0.000469552	0.05622	0.00858	0.01101	0.23671
0(2)-> 3(2) 1	19178.2	521.4	0.000036950	0.00409	0.00150	0.00303	0.06387
0(2)-> 4(2) 1	25365.5	394.2	0.000323858	0.02711	0.01515	0.01643	0.16313
0(2)-> 5(2) 1	26171.3	382.1	0.000013420	0.00109	0.02439	-0.02217	-0.00165
0(2)-> 6(2) 1	27752.2	360.3	0.000007833	0.00060	0.01797	-0.01663	0.00023
0(2)->10(2) 1	37986.2	263.3	0.000000047	0.00000	0.00121	-0.00104	0.00029
0(2)->11(2) 1	38815.8	257.6	0.000000354	0.00002	-0.00161	-0.00124	0.00391
0(2)-> 7(2) 1	39085.2	255.9	0.000006963	0.00038	-0.01411	0.01339	0.00011
0(2)-> 9(2) 1	39545.2	252.9	0.000021365	0.00115	-0.00598	-0.00117	-0.03332
0(2)-> 8(2) 1	39710.1	251.8	0.000004750	0.00025	-0.00810	0.00945	0.00995
0(2)->12(2) 1	42316.0	236.3	0.000003910	0.00020	0.01028	-0.00952	-0.00004
0(2)->13(2) 1	43368.5	230.6	0.000000058	0.00000	-0.00114	-0.00114	-0.00051
0(2)->14(2) 1	44115.9	226.7	0.000003104	0.00015	-0.00882	-0.00832	-0.00159
0(2)->18(2) 1	45086.5	221.8	0.000076326	0.00359	-0.04346	0.04131	0.00024
0(2)->15(2) 1	45647.5	219.1	0.000002400	0.00011	-0.00747	0.00748	-0.00012
0(2)->17(2) 1	45849.3	218.1	0.000013962	0.00065	-0.00004	0.00097	0.02541
0(2)->16(2) 1	46053.5	217.1	0.000004002	0.00018	-0.00193	-0.00151	0.01336
0(2)->19(2) 1	46530.4	214.9	0.000013312	0.00061	0.01790	-0.01693	-0.00071

NEVPT2 TRANSITION ENERGIES

LOWEST ROOT (ROOT 0, MULT 1) = -2322.178494613 Eh -63189.689 eV 1A1g

STATE	ROOT	MULT	DE/a.u.	DE/eV	DE/cm**-1	SYMMETRY
1:	2	3	0.040876	1.112	8971.3	3Eg(1)
2:	0	3	0.042602	1.159	9350.0	3Eg(1)
3:	1	3	0.043031	1.171	9444.2	3A2g
4:	4	3	0.054602	1.486	11983.8	3Eg(2)
5:	3	3	0.055602	1.513	12203.3	3Eg(2)
6:	0	5	0.060716	1.652	13325.7	5B2g
7:	5	3	0.067788	1.845	14877.6	3B2g
8:	1	5	0.068989	1.877	15141.3	5Eg
9:	2	5	0.071728	1.952	15742.4	5Eg
10:	1	1	0.078746	2.143	17282.8	1Eg(1)
11:	2	1	0.080803	2.199	17734.1	1Eg(1)
12:	3	1	0.087382	2.378	19178.2	1A2g
13:	4	1	0.115574	3.145	25365.5	1Eg(2)
14:	9	3	0.119207	3.244	26162.8	
15:	5	1	0.119245	3.245	26171.3	1Eg(2)
16:	8	3	0.120380	3.276	26420.4	
17:	6	3	0.121785	3.314	26728.8	
18:	7	3	0.123029	3.348	27001.7	
19:	6	1	0.126448	3.441	27752.2	1B2g
20:	10	3	0.135609	3.690	29762.8	
21:	11	3	0.137016	3.728	30071.5	
22:	3	5	0.157561	4.287	34580.7	5B1g
23:	14	3	0.158284	4.307	34739.3	
24:	4	5	0.160288	4.362	35179.2	5A1g
25:	12	3	0.161956	4.407	35545.2	
26:	16	3	0.162893	4.433	35750.9	
27:	15	3	0.163148	4.439	35806.9	
28:	13	3	0.166191	4.522	36474.8	
29:	17	3	0.170973	4.652	37524.3	
30:	10	1	0.173078	4.710	37986.2	
31:	18	3	0.174358	4.745	38267.2	
32:	11	1	0.176858	4.813	38815.8	
33:	7	1	0.178085	4.846	39085.2	
34:	19	3	0.179483	4.884	39391.9	
35:	9	1	0.180181	4.903	39545.2	
36:	8	1	0.180933	4.923	39710.1	
37:	12	1	0.192806	5.247	42316.0	
38:	13	1	0.197601	5.377	43368.5	
39:	14	1	0.201007	5.470	44115.9	
40:	18	1	0.205429	5.590	45086.5	
41:	15	1	0.207986	5.660	45647.5	
42:	17	1	0.208905	5.685	45849.3	
43:	16	1	0.209835	5.710	46053.5	
44:	19	1	0.212008	5.769	46530.4	

ORBITAL ORDERING

```
Orbital number (ORCA): 85 | 86| 87  |   88    |   89    |   90   | 91  | ....
Orbital designation  :  L | L | dxy | dxz/dyz | dxz/dyz | dx2-y2 | dz2 | 2nd d-shell
Ground-state occ     :  2 | 2 |  2  |    2    |    2    |    2   |  2  |   00000
Orbital symmetries   :  - | - | b2g |    eg   |    eg   |   b1g  | a1g |   -----
```

CAS-SCF STATES FOR BLOCK 1 MULT= 5 NROOTS= 5

```
ROOT   0:  E=   -2318.2386166993 Eh
      0.91178 [     0]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (b1g)1 (a1g)1   --->   B2g
ROOT   1:  E=   -2318.2303588518 Eh  0.225 eV   1812.4 cm**-1
      0.94733 [   126]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   2:  E=   -2318.2283188587 Eh  0.280 eV   2260.1 cm**-1
      0.90470 [   182]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   3:  E=   -2318.1436498776 Eh  2.584 eV  20842.8 cm**-1
      0.97137 [   203]: 22 1 11 2 1 00000    (b2g)1 (eg)2 (b1g)2 (a1g)1   --->   B1g
ROOT   4:  E=   -2318.1342803735 Eh  2.839 eV  22899.2 cm**-1
      0.96793 [   209]: 22 1 11 1 2 00000    (b2g)1 (eg)2 (b1g)1 (a1g)2   --->   A1g
```

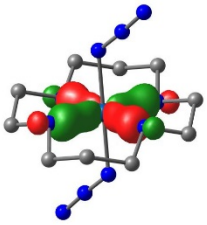
CAS-SCF STATES FOR BLOCK 2 MULT= 3 NROOTS=20

```
ROOT   0:  E=   -2318.2461136133 Eh
      0.41519 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.35186 [   378]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
ROOT   1:  E=   -2318.2448175659 Eh  0.035 eV    284.4 cm**-1
      0.48561 [   378]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
      0.19816 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.17562 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
ROOT   2:  E=   -2318.2443548281 Eh  0.048 eV    386.0 cm**-1
      0.44053 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.41677 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   3:  E=   -2318.2267381431 Eh  0.527 eV   4252.4 cm**-1
      0.40764 [     1]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.39592 [    28]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   4:  E=   -2318.2263822477 Eh  0.537 eV   4330.5 cm**-1
      0.58862 [    29]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.21537 [     0]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   5:  E=   -2318.2104101495 Eh  0.972 eV   7836.0 cm**-1
      0.75192 [   379]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (b1g)0 (a1g)1   --->   B2g
      0.10543 [    36]: 22 2 11 1 1 00000
```

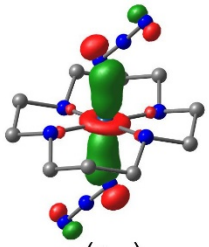
CAS-SCF STATES FOR BLOCK 3 MULT= 1 NROOTS=20

```
ROOT   0:  E=   -2318.2820539100 Eh
      0.88107 [     0]: 22 2 22 0 0 00000    (b2g)2 (eg)4 (b1g)0 (a1g)0   --->   A1g
ROOT   1:  E=   -2318.2026681958 Eh  2.160 eV  17423.2 cm**-1
      0.64232 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.25765 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   2:  E=   -2318.2015535788 Eh  2.191 eV  17667.8 cm**-1
      0.57200 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.33977 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
ROOT   3:  E=   -2318.1993270529 Eh  2.251 eV  18156.4 cm**-1
      0.87367 [   414]: 22 1 22 1 0 00000    (b2g)1 (eg)4 (b1g)1 (a1g)0   --->   A2g
ROOT   4:  E=   -2318.1590176266 Eh  3.348 eV  27003.3 cm**-1
      0.47907 [     1]: 22 2 21 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.27214 [    37]: 22 2 12 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.13324 [   422]: 22 1 21 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   5:  E=   -2318.1557014670 Eh  3.438 eV  27731.2 cm**-1
      0.54056 [    36]: 22 2 12 1 0 00000    (b2g)2 (eg)3 (b1g)1 (a1g)0   --->   Eg
      0.22780 [     2]: 22 2 21 0 1 00000    (b2g)2 (eg)3 (b1g)0 (a1g)1   --->   Eg
      0.12033 [   527]: 22 1 12 1 1 00000    (b2g)1 (eg)3 (b1g)1 (a1g)1   --->   Eg
ROOT   6:  E=   -2318.1476794459 Eh  3.657 eV  29491.8 cm**-1
      0.64259 [   415]: 22 1 22 0 1 00000    (b2g)1 (eg)4 (b1g)0 (a1g)1   --->   B2g
      0.22835 [    44]: 22 2 11 1 1 00000    (b2g)2 (eg)2 (b1g)1 (a1g)1   --->   A1g
```

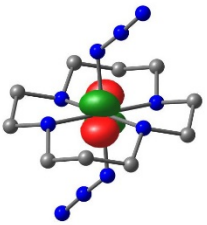
Isosurfaces of CAS orbitals



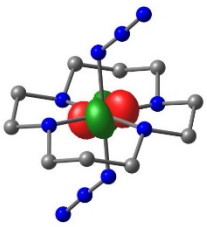
$\sigma(b_{1g})$



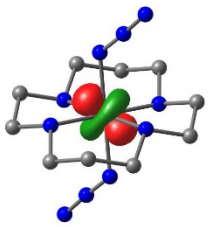
$\sigma(a_{1g})$



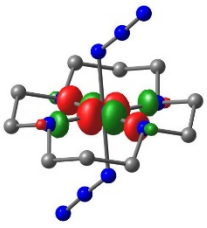
b_{2g}



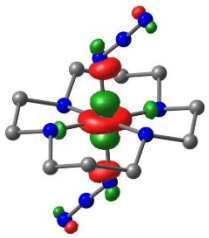
e_g



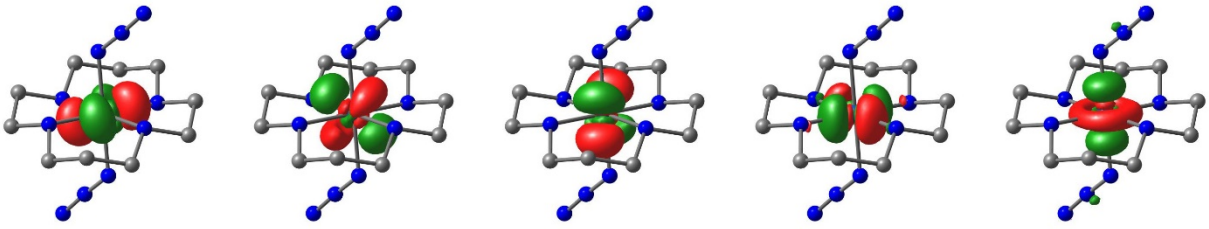
e_g



$\sigma^*(b_{1g})$



$\sigma^*(a_{1g})$



2nd d-shell

Single-crystal X-ray diffraction and comparison with DFT

X-ray data were collected on a Bruker D8 Venture system at 100(2) K using graphite-monochromated $Mo_{K\alpha}$ radiation (λα = 0.71073 Å). The strategy for the data collection was evaluated using APEX3 software.[1] The data were collected by the omega + phi scan techniques and the data were scaled and reduced using SAINT+ and SADABS software.[2,3] The structure was solved by intrinsic phasing using SHELXT-2014/7. and was refined by full matrix least-squares using SHELXL-2014/7. The structure was refined on F^2. Non-hydrogen atoms were refined anisotropically.[4-7] CCDC 1915552 (Compound number) contains the supplementary crystallographic data for this paper.

Table 1. Crystallographic data

Co(cyclam)$(N_3)_2(BF_4)$	
Chemical formula	C10 H24 Cl Co N10 O4
*M*r	442.77
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.4722(6)
b (Å)	9.5461(6)
c (Å)	11.1039(7)
α (°)	79.392(2)
β (°)	80.445(2)
γ (°)	63.255(2)
V (Å^3)	877.34(10)
Z	2
Density (g cm^{-3})	1.676
F(000)	460
Radiation Type	Mo *K*α
μ (mm^{-1})	1.173
Crystal size (mm^3)	0.08 x 0.08 x 0.06
Meas. Refl.	13742
Indep. Refl.	3223
Obsvd. [$I > 2\sigma(I)$] refl.	2653
R_{int}	0.0548
R [$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.0414, 0.0919, 1.117
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.571, -0.644

Table 2. Selected bond lengths (Å) and angles (°) for Co(cyclam)$(N_3)_2(BF_4)$.

Co(cyclam)$(N_3)_2(BF_4)$	
N1-Co1	1.969(3)
N2-Co1	1.977(3)
N50-Co1	1.944(3)
N11-Co2	1.975(3)
N12Co2	1.973(3)
N60-Co1*	1.947(3)

*second structural unit in the crystal

Table 3. Comparison between X-ray and DFT structural parameters (bond lengths in Å, angles and dihedrals in degree). Atom numbering as defined in Figures 3 and 6 of the main paper.

Coordinate	X-ray-structure*	DFT-structure
N(1)–Co and N(8)–Co	1.973	2.012
N(4)–Co and N(11)–Co	1.976	2.009
Co–N(α,1) and Co–N(α,2)	1.946	1.980
N(α,1)–N(β,1) and N(α,2)–N(β,2)	1.188	1.197
N(β,1)–N(γ,1) and N(β,2)–N(γ,2)	1.170	1.148
Co–N(α,1)–N(β,1) and Co–N(α,2)–N(β,2)	127.6	129.6
N(1)–Co–N(4) and N(8)–Co–N(11)	86.1	85.9
N(4)–Co–N(8) and N(1)–Co–N(11)	93.9	94.1
N(α,1)–N(β,1)–N(γ,1) and N(α,2)–N(β,2)–N(γ,2)	175.9	176.5
N(11)–Co–N(α,1)–N(β,1)	–65	–65
N(4)–Co–N(α,2)–N(β,2)	+65	+65

*second structural unit in the crystal

References

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[5] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, ShelXle: a Qt user interface for SHELXLirger, *J. Appl. Cry*st. **2011**, 44, 1281;

[6] G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112

[7] G. M. Sheldrick, Acta Cryst. **2015**, *C71*, 3.