Supplementary Information

Cobalt analogues of Roussin's red salt esters: a density functional study

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Table S1. BP86/6-311G(d) electronic energies and thermodynamic corrections calculated for the singlet $Co_2(NO)_4(SCH_3)_2$ structures. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		Sum of electronic and zero-point Energies		Sum of electronic and thermal Enthalpies		Sum of electronic and thermal Free Energies	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	–4162.324123	0.0	–4162.214990	0.1	–4162.193777	0.2	–4162.269905	0.1
O-dd-1	–4162.323665	0.3	–4162.215196	0.0	–4162.193943	0.1	–4162.270025	0.0
O-TS-1	–4162.323209	0.6	–4162.214490	0.4	–4162.194028	0.0	–4162.267322	1.7
B-d-1	–4162.311128	8.2	–4162.202870	7.7	–4162.181843	7.6	–4162.255780	8.9
B-u-1	–4162.308826	9.6	–4162.200784	9.0	–4162.179762	9.0	–4162.253686	10.3
Iso-1	–4162.260142	40.1	–4162.152493	39.3	–4162.131098	39.5	–4162.206447	39.9

Table S2. BP86/6-311G(d) electronic energies and thermodynamic corrections calculated for the relevant singlet $Co_2(NO)_4(SCH_3)_2$ structures including corrections for the solvent effects. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		Sum of electronic and zero-point Energies		Sum of electronic and thermal Enthalpies		Sum of electronic and thermal Free Energies	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	–4162.329890	0.0	–4162.221438	0.4	–4162.200645	0.4	–4162.275630	0.3
O-dd-1	–4162.329860	0.0	–4162.222022	0.0	–4162.201240	0.0	–4162.276139	0.0
B-d-1	–4162.320758	5.7	–4162.212618	5.9	–4162.192261	5.6	–4162.263663	7.8
B-u-1	–4162.320140	6.1	–4162.212308	6.1	–4162.191802	5.9	–4162.263335	8.0
Iso-1	–4162.267155	39.4	–4162.159921	39.0	–4162.139009	39.1	–4162.212767	39.8

Table S3. M06-L/6-311G(d) electronic energies and thermodynamic corrections calculated for the singlet $Co_2(NO)_4(SCH_3)_2$ structures. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		Sum of electronic and zero-point Energies		Sum of electronic and thermal Enthalpies		Sum of electronic and thermal Free Energies	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	–4161.502005	0.0	–4161.389440	0.0	–4161.369686	0.0	–4161.440422	0.0
O-dd-1	–4161.500846	0.7	–4161.387731	1.1	–4161.367628	1.3	–4161.438120	1.4
O-uu-1	–4161.500758	0.8	–4161.388065	0.9	–4161.367637	1.3	–4161.439104	0.8
O-TS-1	–4161.497960	2.6	–4161.386231	2.0	–4161.366844	1.8	–4161.438272	1.3
B-d-1	–4161.485068	10.6	–4161.373471	10.0	–4161.352721	10.6	–4161.425606	9.3
B-u-1	–4161.482535	12.2	–4161.371304	11.4	–4161.350540	12.0	–4161.422978	10.9
Iso-1	–4161.437481	40.5	–4161.325944	39.8	–4161.305320	40.4	–4161.377282	39.6

Table S4. BP86/6-311G(d) electronic energies and thermodynamic corrections calculated for the singlet $Co_2(NO)_4(SCF_3)_2$ structures. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		**Sum of electronic and zero-point Energies**		**Sum of electronic and thermal Enthalpies**		**Sum of electronic and thermal Free Energies**	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	–4757.952947	0.0	–4757.890125	0.0	–4757.864761	0.4	–4757.952326	0.0
O-TS-1	–4757.952600	0.2	–4757.889917	0.1	–4757.865385	0.0	–4757.949773	1.6
O-dd-1	–4757.952511	0.3	–4757.889757	0.2	–4757.864360	0.6	–4757.952058	0.2
B-u-1	–4757.941747	7.0	–4757.879132	6.9	–4757.854184	7.0	–4757.939366	8.1
B-d-1	–4757.938721	8.9	–4757.875976	8.9	–4757.851063	9.0	–4757.936132	10.2
Iso-1	–4757.888229	40.6	–4757.826590	39.9	–4757.801003	40.4	–4757.888492	40.1

Table S5. BP86/6-311G(d) electronic energies and thermodynamic corrections calculated for the singlet $Co_2(NO)_4(SCF_3)_2$ structures including corrections for the solvent effects. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		**Sum of electronic and zero-point Energies**		**Sum of electronic and thermal Enthalpies**		**Sum of electronic and thermal Free Energies**	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	-4757.959428	0.0	-4757.897437	0.0	-4757.872647	0.0	-4757.958101	0.4
O-dd-1	-4757.959180	0.2	-4757.897379	0.0	-4757.872484	0.1	-4757.958669	0.0
B-u-1	-4757.953577	3.7	-4757.891428	3.8	-4757.867271	3.4	-4757.949118	6.0
B-d-1	-4757.952147	4.6	-4757.890121	4.6	-4757.865879	4.2	-4757.948122	6.6
Iso-1	-4757.896058	39.8	-4757.835351	39.0	-4757.810267	39.1	-4757.896255	39.2

Table S6. BP86/6-311G(d) electronic energies and thermodynamic corrections calculated for the relevant $Co_2(NO)_4(SC_4H_9)_2$ structures. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		**Sum of electronic and zero-point Energies**		**Sum of electronic and thermal Enthalpies**		**Sum of electronic and thermal Free Energies**	
	total	relative	total	relative	total	relative	total	relative
O-ud-1	–4398.254402	0.0	–4397.981556	0.0	–4397.952171	0.0	–4398.043912	0.0
O–dd–1	–4398.253241	0.7	–4397.980367	0.7	–4397.951035	0.7	–4398.041656	1.4
B–u–1	–4398.235778	11.7	–4397.963204	11.5	–4397.934278	11.2	–4398.024846	12.0
B–d–1	–4398.236531	11.2	–4397.964215	10.9	–4397.935122	10.7	–4398.026460	11.0
Iso–1	–4398.190170	40.3	–4397.918650	39.5	–4397.889055	39.6	–4397.980799	39.6

Table S7. BP86/6–311G(d) electronic energies and thermodynamic corrections calculated for the relevant singlet $Co_2(NO)_4(SC_4H_9)_2$ structures including corrections for the solvent effects. Total energies in a.u., relative energies in kcal mol^{-1}.

	Electronic Energies		**Sum of electronic and zero–point Energies**		**Sum of electronic and thermal Enthalpies**		**Sum of electronic and thermal Free Energies**	
	total	relative	total	relative	total	relative	total	relative
O–ud–1	–4398.259750	0.0	–4397.987667	0.0	–4397.959044	0.0	–4398.048424	0.0
O–dd–1	–4398.259127	0.4	–4397.987344	0.2	–4397.958588	0.3	–4398.047765	0.4
B–d–1	–4398.243942	9.9	–4397.972203	9.7	–4397.943995	9.4	–4398.032015	10.3
B–u–1	–4398.246883	8.1	–4397.974747	8.1	–4397.946698	7.7	–4398.033842	9.2
Iso–1	–4398.196749	39.5	–4397.925913	38.8	–4397.897141	38.8	–4397.985999	39.2

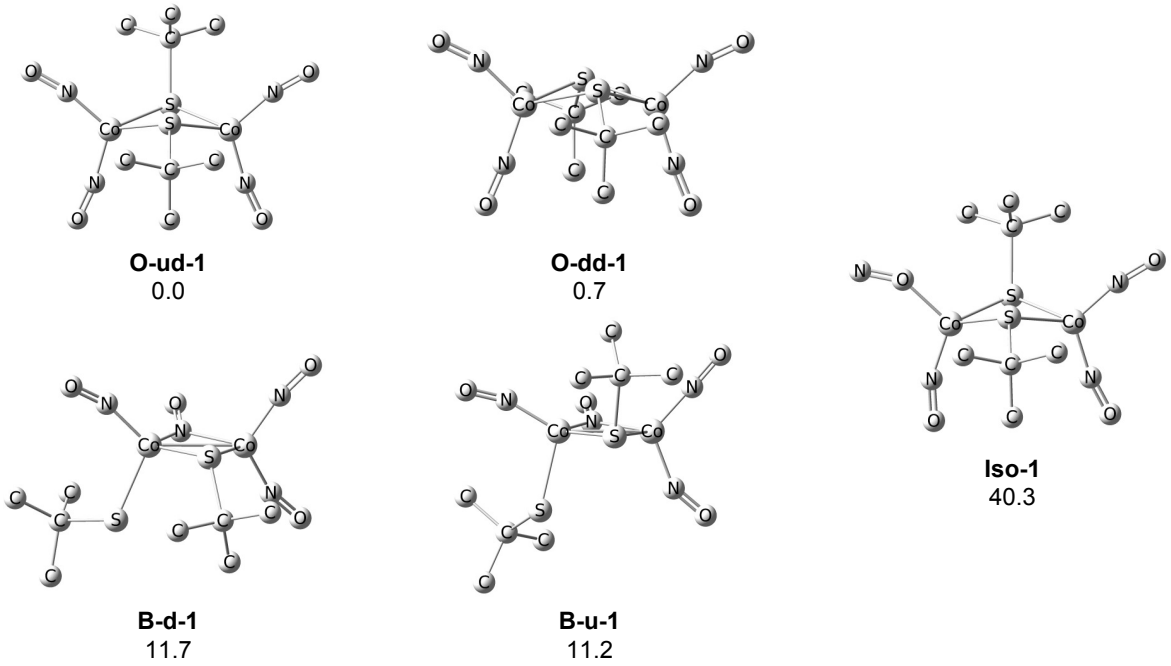

Figure S1. BP86/6–311G(d) optimized $Co_2(NO)_4(SC_4H_9)_2$ geometries without corrections for the solvent effects. Hydrogen atoms are not shown for clarity.

Table S8. BP86/6-311G(d) structural parameters (Å), HOMO-LUMO gaps (eV), imaginary frequencies (cm^{-1}) and point groups of the $Co_2(NO)_4(SC_4H_9)_2$ structures without corrections for the solvent effects.

	Co–Co	Co–S[a]	Co–N[b]	N–O[c]	HOMO-LUMO	Imaginary freq.	
O-ud-1	3.418	2.339	1.642	1.175	1.6	none	C_s
		2.293	1.640	1.173			
O-dd-1	3.425	2.311	1.651	1.172	1.7	none	C_2
		2.310	1.633	1.177			
B-d-1	2.630	2.236	1.650	1.170	0.6	none	C_1
		2.270	*1.729*	*1.200*			
		2.200	*1.997*				
B-u-1	2.575	2.281	1.656	1.172	0.7	none	C_1
		2.227	*1.725*	*1.202*			
		2.214	*1.955*				

[a] Terminal Co–S distances in *italics*. [b] Terminal Co–N(O) distances are averaged for the butterfly type structures, bridging Co–N(O) distances in *italics*. [c] Terminal N–O distances are averaged for the butterfly type structures, bridging N–O distances in *italics*.

Table S9. BP86/6–311G(d) atomic charge distributions from natural population analysis and relative charge differences for **O–ud–1** $Co_2(NO)_4(SR)_2$ (R = CH_3, CF_3).

R = CH_3			R = CF_3			charge difference
Atom	**No**	**NPA charge**	**Atom**	**No**	**NPA charge**	
Co	1	0.80	Co	1	0.80	0.0
S	2	–0.29	S	2	–0.37	**–0.1**
Co	3	0.80	Co	3	0.80	0.0
S	4	–0.25	S	4	–0.35	**–0.1**
N	5	–0.06	N	5	–0.03	0.0
O	6	–0.16	O	6	–0.13	0.0
N	7	–0.07	N	7	–0.04	0.0
O	8	–0.16	O	8	–0.13	0.0
N	9	–0.06	N	9	–0.03	0.0
O	10	–0.16	O	10	–0.13	0.0
N	11	–0.07	N	11	–0.04	0.0
O	12	–0.16	O	12	–0.13	0.0
C	13	–0.70	C	13	0.91	**1.6**
C	14	–0.71	C	14	0.91	**1.6**
H	15	0.21	F	15	–0.35	–0.6
H	16	0.21	F	16	–0.34	–0.5
H	17	0.21	F	17	–0.34	–0.5
H	18	0.21	F	18	–0.34	–0.5
H	19	0.20	F	19	–0.35	–0.6
H	20	0.21	F	20	–0.34	–0.5

Table S10. BP86/6–311G(d) atomic charge distributions from natural population analysis and relative charge differences for **O–dd–1** $Co_2(NO)_4(SR)_2$ (R = CH_3, CF_3).

R = CH_3			R = CF_3			charge difference
Atom	**No**	**NPA charge**	**Atom**	**No**	**NPA charge**	
Co	1	0.79	Co	1	0.80	0.0
S	2	–0.25	S	2	–0.37	**–0.1**
Co	3	0.79	Co	3	0.80	0.0
S	4	–0.25	S	4	–0.37	**–0.1**
N	5	–0.04	N	5	–0.03	0.0
O	6	–0.16	O	6	–0.13	0.0
N	7	–0.09	N	7	–0.04	0.0
O	8	–0.19	O	8	–0.13	**0.1**
N	9	–0.04	N	9	–0.03	0.0
O	10	–0.16	O	10	–0.13	0.0
N	11	–0.09	N	11	–0.04	0.0
O	12	–0.19	O	12	–0.13	**0.1**
C	13	–0.70	C	13	0.92	**1.6**
C	14	–0.70	C	14	0.92	**1.6**
H	15	0.21	F	15	–0.33	–0.5
H	16	0.21	F	16	–0.33	–0.5
H	17	0.21	F	17	–0.33	–0.5
H	18	0.21	F	18	–0.35	–0.6
H	19	0.21	F	19	–0.35	–0.6
H	20	0.21	F	20	–0.33	–0.5

Table S11 – BP86/6–311G(d) atomic charge distributions from natural population analysis and relative charge differences for **B–d–1** $Co_2(NO)_4(SR)_2$ (R = CH_3, CF_3).

R = CH_3			R = CF_3			charge difference
Atom	**No**	**NPA charge**	**Atom**	**No**	**NPA charge**	
Co	1	0.83	Co	1	0.82	0.0
S	2	–0.25	S	2	–0.36	**–0.1**
Co	3	0.78	Co	3	0.78	0.0
S	4	–0.27	S	4	–0.30	0.0
N	5	–0.02	N	5	0.00	0.0
O	6	–0.13	O	6	–0.10	0.0
N	7	–0.04	N	7	–0.02	0.0
O	8	–0.13	O	8	–0.11	0.0
N	9	–0.05	N	9	–0.02	0.0
O	10	–0.17	O	10	–0.12	**0.1**
N	11	–0.22	N	11	–0.20	0.0
O	12	–0.19	O	12	–0.15	0.0
C	13	–0.70	C	13	0.93	**1.6**
C	14	–0.71	C	14	0.89	**1.6**
H	15	0.20	F	15	–0.35	–0.6
H	16	0.21	F	16	–0.34	–0.6
H	17	0.20	F	17	–0.35	–0.6
H	18	0.22	F	18	–0.32	–0.5
H	19	0.21	F	19	–0.33	–0.5
H	20	0.23	F	20	–0.33	–0.6

Table S12 – BP86/6–311G(d) atomic charge distributions from natural population analysis and relative charge differences for **B–u–1** $Co_2(NO)_4(SR)_2$ (R = CH_3, CF_3).

R = CH_3			R = CF_3			charge difference
Atom	**No**	**NPA charge**	**Atom**	**No**	**NPA charge**	
Co	1	0.82	Co	1	0.82	0.0
S	2	–0.21	S	2	–0.31	**–0.1**
Co	3	0.76	Co	3	0.76	0.0
S	4	–0.22	S	4	–0.31	**–0.1**
N	5	–0.01	N	5	0.01	0.0
O	6	–0.12	O	6	–0.10	0.0
N	7	–0.05	N	7	–0.02	0.0
O	8	–0.15	O	8	–0.11	0.0
N	9	–0.06	N	9	–0.02	0.0
O	10	–0.17	O	10	–0.12	0.0
N	11	–0.23	N	11	–0.20	0.0
O	12	–0.19	O	12	–0.15	0.0
C	13	–0.71	C	13	0.91	**1.6**
C	14	–0.72	C	14	0.89	**1.6**
H	15	0.20	F	15	–0.35	–0.6
H	16	0.21	F	16	–0.34	–0.6
H	17	0.20	F	17	–0.36	–0.6
H	18	0.22	F	18	–0.33	–0.5
H	19	0.20	F	19	–0.35	–0.6
H	20	0.21	F	20	–0.33	–0.5

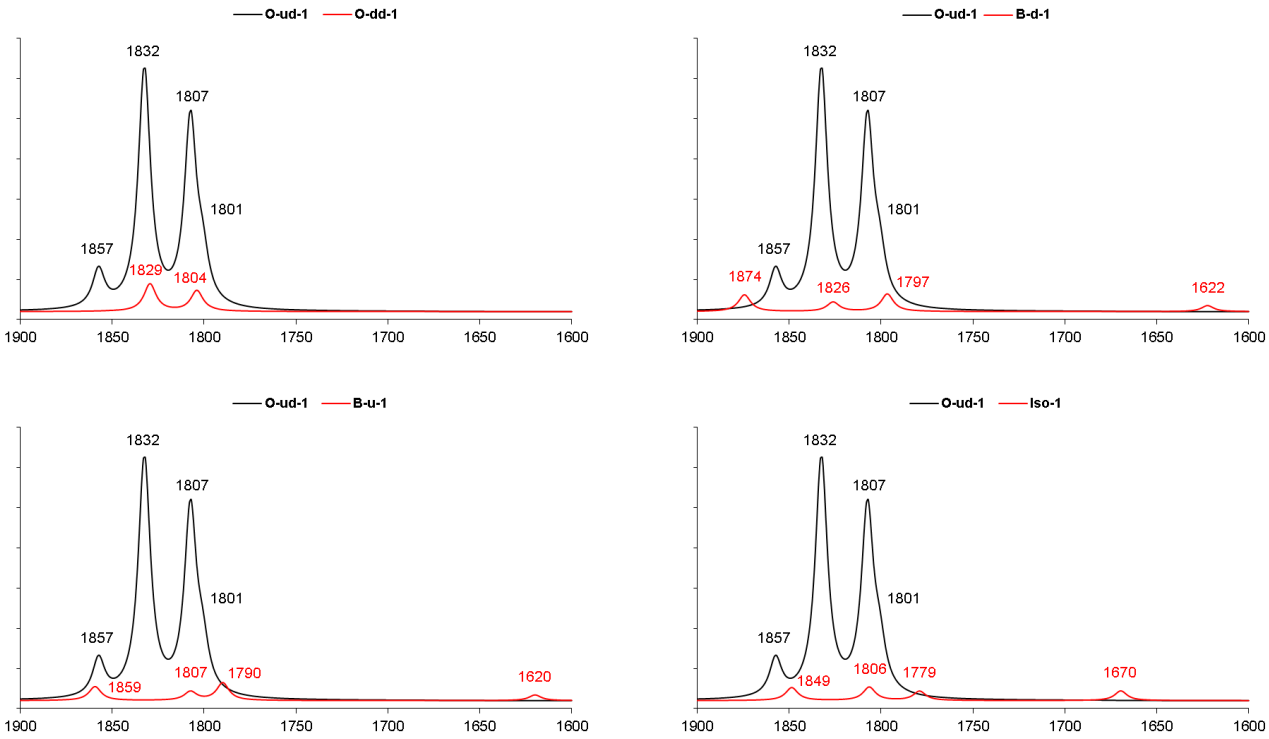

Figure S2. BP86/6–311G(d) superimposed theoretical IR spectra of the **O–ud–1** $Co_2(NO)_4(SC_4H_9)_2$ structures (shown in black) with the corresponding theoretical IR spectra of **O–dd–1**, **B–d–1**, **B–u–1** and **Iso–1** (shown in red). The spectra of **O–dd–1**, **B–d–1**, **B–u–1** and **Iso–1** have been rescaled 10:1 (according to ref. 7).