Table S1 Parameters (absorbance α_i, wavenumber v_i and half-width Δ_i) obtained from Gaussian deconvolution of the visible-NIR spectra of cobalamins (X-cbl)

Ligand X	Solvent	Band	α_i	Error	$\overline{\nu}_i / cm^{-1}$	Error	Δ_i/cm^{-1}	Error
F^-	CH_3OH	1	0.6289	0.0026	18462.3	0.6	436.81	1.05
		2	0.0774	0.0133	18560.0	436.8	2099.16	129.03
		3	1.5622	0.0184	19531.8	2.1	1061.68	4.43
		4	0.3258	0.0039	21551.0	2.7	630.14	3.63
		5	0.7674	0.0028	24069.2	12.0	1725.25	13.16
Cl^-	H_2O	1	0.0984	0.0005	14562.9	17.8	1971.00	9.71
		2	0.6834	0.0017	18299.2	0.5	479.44	0.65
		3	1.4240	0.0066	19397.5	2.4	1129.10	2.18
		4	0.3578	0.0038	21363.9	3.0	719.58	3.27
		5	0.1754	0.0022	23924.0	1.7	397.38	2.94
		6	0.7410	0.0155	26430.1	224.1	3302.09	154.43
Cl^-	CH_3OH	1	0.1113	0.0003	15340.6	12.2	1767.69	9.56
		2	0.6977	0.0029	18301.8	0.8	415.17	1.09
		3	1.4836	0.0031	19279	6.9	1045.21	3.09
		4	0.609	0.0046	21471.1	9.4	950.78	10.12
		5	0.693	0.0014	24091.7	4.2	798.62	6.88
		6	0.327	0.0147	25127.3	21.5	299.8	13.29
Br^-	H_2O	1	0.1030	0.0008	13810.8	9.6	1793.72	9.23
		2	0.6593	0.0016	18076.7	0.4	440.26	0.54
		3	1.4120	0.0018	19076.1	2.3	985.35	1.33
		4	0.4671	0.0023	21001.5	3.1	802.80	2.95
		5	0.2031	0.0011	23650.5	0.9	437.81	1.84
		6	3.1075	0.3063	36276.8	720.1	6846.52	190.02
Br^-	CH_3OH	1	0.1349	0.0002	14621.4	4.0	1650.73	4.57
		2	0.7299	0.0015	18078.7	0.5	392.54	0.64
		3	1.3616	0.0014	19098.8	2.0	1010.33	1.15
		4	0.3712	0.0026	21098.7	2.8	680.98	3.55
		5	0.1532	0.0013	23501.2	2.2	339.02	3.03
		6	0.7404	0.0039	25620.4	49.0	2542.99	34.28
I^-	H_2O	1	0.1963	0.0002	13388.2	3.0	1642.29	2.42
		2	0.6959	0.0024	17592.2	0.4	411.82	0.67
		3	1.0915	0.0015	18636.7	1.7	855.37	1.83
		4	0.2460	0.0011	20391.7	2.9	624.40	2.45
		5	0.0836	0.0007	22707.8	2.3	410.63	3.61
		6	1.0041	0.0002	24541.5	8.6	3763.57	8.59
I^-	CH_3OH	1	0.1993	0.0002	13758.3	2.2	1505.24	1.65
		2	0.6943	0.0016	17643.3	0.2	398.39	0.44
		3	1.1671	0.0011	18720.6	0.9	858.88	1.38
		4	0.2653	0.0008	20480.4	1.7	592.20	1.59
		5	0.0537	0.0005	22695.1	2.4	381.80	3.97
		6	0.7993	0.0004	23373.1	4.7	3237.70	6.44
H_2O	H_2O	1	0.0477	0.0003	15271.3	26.6	1687.77	21.16
		2	0.6077	0.0028	18718.2	1.2	509.77	1.55
		3	1.6138	0.0010	20007.9	5.4	1325.01	2.85
		4	0.2939	0.0058	22062.9	5.8	712.38	8.63
		5	0.7549	0.0007	24501.5	2.5	1033.24	6.31

H_2O	CH_3OH/	1	0.0490	0.0003	15576.8	35.0	1851.49	24.76
	H_2O 80/20	2	0.5982	0.0031	18745.9	1.2	522.48	1.62
		3	1.6150	0.0011	20014.0	5.6	1289.69	2.92
		4	0.3282	0.0059	22109.3	5.8	746.73	8.68
		5	0.7503	0.0006	24545.8	2.5	1014.65	6.74
H_2O	CH_3CN/	1	0.0535	0.0003	15417.6	30.6	1836.95	22.11
	H_2O 80/20	2	0.6023	0.0032	18676.6	1.3	543.53	1.69
		3	1.6212	0.0011	19986.6	5.6	1315.36	2.88
		4	0.2940	0.0056	22093.0	6.0	740.64	9.10
		5	0.7479	0.0006	24538.5	2.4	1008.10	6.27
Ligand X	**Solvent**	**Band**	**α_i**	**Error**	**$\bar{\nu}_i/cm^{-1}$**	**Error**	**Δ_i/cm^{-1}**	**Error**
CH_3OH	CH_3OH	1	0.0853	0.0002	15427.2	12.3	1865.26	9.45
		2	0.4510	0.0035	18354.0	1.2	458.92	1.67
		3	1.4729	0.0088	19233.2	9.6	984.26	3.25
		4	0.8326	0.0085	21167.6	14.3	1041.16	9.96
		5	0.7448	0.0004	24444.7	2.2	1161.45	5.84
$(CH_3)_2SO$	$(CH_3)_2SO$	1	0.0994	0.0004	15340.3	12.9	1436.82	10.94
		2	0.6239	0.0033	18320.3	1.1	417.75	1.55
		3	1.5391	0.0014	19344.3	5.3	1062.66	2.80
		4	0.6207	0.0050	21430.4	5.2	791.48	5.52
		5	0.7601	0.0008	24312.1	3.0	1227.61	7.62
CH_3COOH	CH_3COOH	1	0.1054	0.0003	15237.5	15.3	1750.10	12.39
		2	0.6905	0.0031	18303.1	1.0	426.44	1.35
		3	1.3898	0.0013	19362.2	4.9	1086.82	2.74
		4	0.4691	0.0039	21461.8	5.2	751.50	5.58
		5	0.6257	0.0008	24303.3	3.2	1166.07	7.10
OH^-	H_2O	1	0.7195	0.0018	18327.4	0.5	455.08	0.72
		2	1.5363	0.0047	19360.7	1.3	1031.31	1.66
		3	0.6238	0.0033	23280.8	94.5	3165.27	35.04
		4	0.2145	0.0028	21413.6	2.6	536.24	3.57
		5	0.2149	0.0152	23758.4	8.7	392.62	8.73
		6	0.2408	0.0136	25022.9	35.7	735.32	88.99
SCN^-/NCS^-	H_2O	1	0.1130	0.0002	15332.5	9.2	1925.31	5.82
		2	0.7287	0.0029	18138.4	0.7	618.81	0.97
		3	1.3488	0.0011	19497.1	3.3	1187.89	2.03
		4	0.2801	0.0024	21385.0	2.6	690.95	2.85
		5	0.7663	0.0002	24504.0	2.0	1562.86	3.26
SCN^-/NCS^-	CH_3OH	1	0.1007	0.0004	15695.7	19.5	1882.09	11.14
		2	0.6188	0.0028	18258.8	0.9	565.87	1.24
		3	1.3791	0.0013	19542.6	4.0	1236.34	2.38
		4	0.2674	0.0033	21539.9	3.8	696.84	4.55
		5	0.8284	0.0003	24561.8	3.1	1522.28	5.20
$SC(NH_2)_2$	H_2O	1	0.1447	0.0002	14722.5	3.9	1710.02	2.83
		2	0.4621	0.0016	17825.3	0.6	453.89	0.83
		3	1.3185	0.0017	18809.7	2.6	1027.87	1.05
		4	0.7629	0.0003	24839.5	11.4	2955.35	17.97
		5	0.4158	0.0032	20764.1	3.0	765.63	3.35
		6	0.0754	0.0006	23152.7	2.2	330.33	2.97
$SC(NH_2)_2$	CH_3OH	1	0.1363	0.0001	14738.1	2.7	1614.66	1.96
		2	0.5223	0.0009	17950.2	0.4	465.97	0.50

		3	1.2040	0.0013	18994.4	1.3	1089.09	0.70
		4	0.2624	0.0014	20955.4	1.5	647.62	2.16
		5	0.0846	0.0005	23208.3	1.6	350.44	2.08
		6	0.7177	0.0003	24962.7	11.3	3035.73	13.77
SO_3^{2-}	H_2O	1	0.0936	0.0296	18967.6	690.2	2011.19	188.76
		2	0.7641	0.0039	18145.7	0.5	446.42	0.94
		3	1.7290	0.0320	19331.0	3.6	976.28	5.90
		4	0.5179	0.0167	21166.9	4.4	765.89	5.26
		5	1.1357	0.0068	24043.4	16.9	1615.16	14.33
$S_2O_3^{2-}$	H_2O	1	0.1230	0.0044	15585.3	42.4	1541.09	31.18
		2	0.9836	0.0599	17957.9	32.7	687.06	8.38
		3	0.7133	0.2022	19061.0	35.0	730.86	55.57
		4	0.6004	0.0647	20365.7	224.5	1069.85	148.05
		5	0.1654	0.0303	22877.0	81.6	845.94	69.98
		6	1.4849	0.2780	32021.4	1515.7	6494.90	349.57
Ligand X	**Solvent**	**Band**	**α_i**	**Error**	**$\bar{\nu}_i / cm^{-1}$**	**Error**	**Δ_i/cm^{-1}**	**Error**
$SeCN^-$	H_2O	1	0.2059	0.0001	14553.2	1.4	1584.68	1.32
		2	0.4473	0.0014	17573.2	0.5	422.47	0.68
		3	1.4768	0.0040	18451.7	3.9	914.61	1.26
		4	0.7015	0.0046	20269.1	6.4	970.22	5.58
		5	0.1540	0.0010	22995.6	1.1	395.33	1.87
		6	0.9073	0.0002	24595.7	2.9	1995.93	7.53
$SeCN^-$	CH_3OH	1	0.1880	0.0001	14691.8	1.4	1639.63	1.28
		2	0.3858	0.0012	17639.5	0.5	417.49	0.65
		3	1.2885	0.0045	18511.1	4.0	903.89	1.23
		4	0.6567	0.0043	20287.0	6.9	996.03	5.94
		5	0.1381	0.0009	23042.1	1.0	401.53	1.84
		6	0.8038	0.0002	24610.5	2.8	1926.38	7.45
OCN^-	H_2O	1	0.0550	0.0005	15667.5	29.8	1030.06	31.73
		2	0.6176	0.0042	18328.2	1.3	458.28	1.95
		3	1.7088	0.0015	19404.6	5.4	1200.07	3.59
		4	0.5231	0.0058	21622.4	5.3	784.31	6.59
		5	0.8068	0.0008	24301.6	2.6	1137.17	6.95
OCN^-	CH_3OH	1	0.0719	0.0008	15807.3	33.8	1035.24	30.98
		2	0.5991	0.0049	18364.0	1.6	433.19	2.30
		3	1.7267	0.0019	19405.7	7.5	1198.37	5.11
		4	0.5465	0.0074	21673.0	8.8	846.42	9.67
		5	0.8012	0.0010	24367.9	2.9	966.11	6.56
NO_2^-	H_2O	1	0.1361	0.0018	16097.2	74.0	1650.20	64.68
		2	0.5956	0.0048	18541.1	1.5	409.50	2.18
		3	1.7026	0.0456	19508.0	33.4	1176.25	14.70
		4	0.6352	0.0353	21718.0	97.0	1242.71	58.02
		5	0.8324	0.0088	24306.1	7.6	615.87	8.89
		6	0.4559	0.0398	25153.1	37.0	280.06	22.19
N_3^-	H_2O	1	0.1187	0.0010	15630.4	10.6	1273.47	6.27
		2	0.6601	0.0018	18246.4	0.6	445.43	0.79
		3	1.5668	0.0070	19205.8	2.1	1116.92	1.90
		4	0.3018	0.0035	21266.3	2.6	624.82	3.53
		5	0.1603	0.0027	23716.6	2.6	401.51	4.56
		6	0.9443	0.0091	25837.3	131.2	3167.76	103.57