Probing the nature of the Co(III) ion in cobalamins: a comparison of the reaction of aquacobalamin (vitamin B_{12a}) and 10-chloroaquacobalmin with some anionic and *N*-donor ligands

Leanne Knapton and Helder M. Marques*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, PO Wits, Johannesburg, 2050, South Africa.

E-mail: hmarques@aurum.chem.wits.ac.za

Supplementary Material

Table S1. Rate constants, corrected for pH, for the reaction of pyridine with 10–Cl–H_2OCbl^+, (I = 2.2 mol dm^{-3}).

Temperature /ºC	[pyridine]/mol dm^{-3}	k_{cor} /s^{-1}
10.04	0.2000	0.6163(9)
	0.3000	0.7084(9)
	0.4000	0.779(1)
	0.5000	0.8091(9)
	0.6000	0.838(1)
	0.7000	0.847(1)
	0.8000	0.855(4)
15.01	0.1250	1.067(3)
	0.2000	1.177(1)
	0.3000	1.324(1)
	0.4000	1.432(1)
	0.5000	1.494(1)
	0.6000	1.531(1)
	0.7000	1.566(3)
19.96	0.1250	2.039(3)
	0.2000	2.292(3)
	0.3000	2.503(1)
	0.4000	2.657(3)
	0.5000	2.803(4)
	0.6000	2.884(3)
	0.7000	2.916(3)
	0.8000	2.976(3)
24.97	0.0250	2.94(1)
	0.0500	3.11(1)
	0.0750	3.33(1)
	0.1000	3.467(9)
	0.1250	3.62(1)
	0.2000	4.053(5)
	0.3000	4.450(5)
	0.4000	4.743(5)
	0.5000	4.963(5)
	0.6000	5.040(7)
	0.7000	5.076(5)
	0.8000	5.138(4)

Table S2. Rate constants, corrected for pH, for the reaction of pyridine with H_2OCbl^+, (I = 2.2 mol dm^{-3}).

Temperature /ºC	[pyridine]/mol dm^{-3}	k_{cor} /s^{-1}
10.04	0.0500	0.5616(5)
	0.1000	0.7549(5)
	0.2000	1.2123(7)
	0.3000	1.479(1)
	0.4000	1.737(1)
	0.5000	1.879(1)
	0.6000	1.986(2)
15.00	0.0500	1.0857(7)
	0.1000	1.467(1)
	0.2000	2.217(1)
	0.3000	2.756(1)
	0.4000	3.187(2)
	0.5000	3.542(2)
	0.6000	3.743(4)
	0.7000	3.970(4)
	0.8000	4.017(5)
	0.9000	4.066(6)
	1.0000	4.092(6)
25.02	0.0500	3.640(2)
	0.1000	4.829(2)
	0.2000	7.267(5)
	0.3000	8.63(1)
	0.4000	10.288(9)
	0.5000	10.89(1)
	0.6000	11.80(1)
	0.7000	12.39(1)
	0.8000	12.43(1)
	0.9000	12.64(1)
	1.0000	12.71(1)
29.87	0.0500	6.69(3)
	0.1000	8.93(6)
	0.2000	13.0(1)
	0.3000	16.29(1)
	0.4000	18.65(1)
	0.5000	19.82(1)
	0.6000	21.32(1)
	0.7000	21.97(1)
	0.8000	22.38(1)
	0.9000	22.85(1)

Table S3. Rate constants, corrected for pH, for the reaction of azide with 10–Cl–H_2OCbl^+, (I = 2.2 mol dm^{-3}).

Temperature /ºC	$[N_3^-]$/mol dm^{-3}	k_{cor} /s^{-1}
5.0	0.0999	5.17(1)
	0.3000	15.34(3)
	0.4002	20.80(3)
	0.5001	26.78(5)
	0.6002	30.45(5)
	0.8001	39.16(5)
	0.9000	44.1(1)
10.1	0.0999	8.61(4)
	0.2999	23.50(4)
	0.4000	31.17(5)
	0.5000	39.6(2)
	0.6000	45.1(3)
	0.8000	66.1(2)
	0.9000	72.9(2)
15.0	0.1002	10.77(2)
	0.2999	34.54(8)
	0.4000	45.25(7)
	0.5000	57.5(1)
	0.6000	66.66(7)
	0.8000	89.9(2)
	0.9000	100.2(2)
24.9	0.2999	69.5(1)
	0.4000	93.5(1)
	0.5000	113.6(2)
	0.6000	136.2(2)
	0.8000	179.8(5)
	0.9000	200.8(3)

Table S4. Rate constants, corrected for pH, for the reaction of azide with H_2OCbl^+, (I = 2.2 mol dm^{-3}).

Temperature /ºC	$[N_3^-]$/mol dm^{-3}	k_{cor} /s^{-1}
5.0	0.01004	0.623(1)
	0.02004	1.1263(9)
	0.02998	1.676(2)
	0.04000	2.099(2)
	0.05002	3.348(3)
	0.06000	3.592(2)
	0.07001	4.112(4)
	0.07999	4.750(3)
	0.1000	5.732(4)
15.0	0.01004	1.821(4)
	0.02004	3.694(8)
	0.02998	5.170(7)
	0.04000	6.462(7)
	0.05002	9.468(8)
	0.06000	10.90(2)
	0.07001	11.61(2)
	0.07999	14.11(2)
	0.1000	16.89(2)
25.0	0.01004	4.812(7)
	0.02998	13.790(8)
	0.04000	17.50(2)
	0.06000	27.55(2)
	0.07001	29.16(2)
	0.07999	36.52(5)
	0.1000	42.58(4)
34.9	0.01004	13.75(2)
	0.02004	26.45(7)
	0.02998	38.38(5)
	0.04000	51.2(2)
	0.05002	69.4(8)
	0.06000	75.36(7)
	0.07001	84.00(6)
	0.07999	95.2(2)
	0.1000	108.1(4)

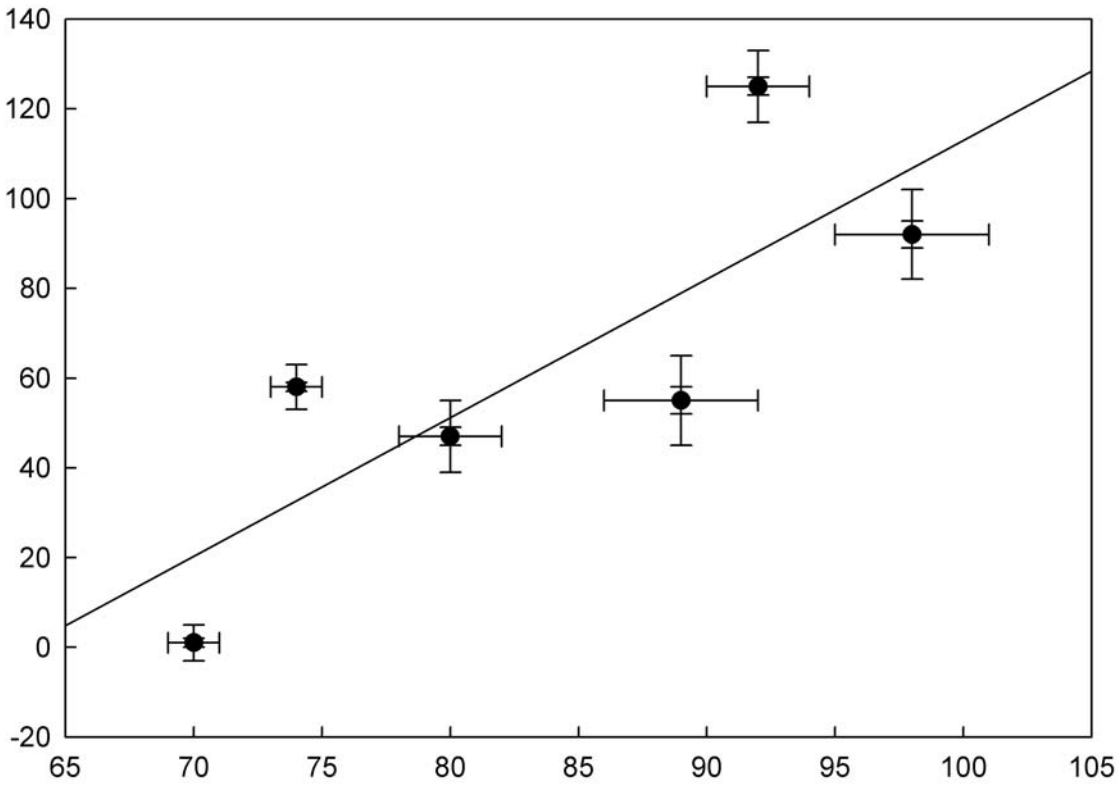

Figure S1. The compensation effect between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reactions between py (k_4 and k_{-4}) and N_3^- (k_4), and 10−Cl−H_2OCbl^+ and H_2OCbl^+.

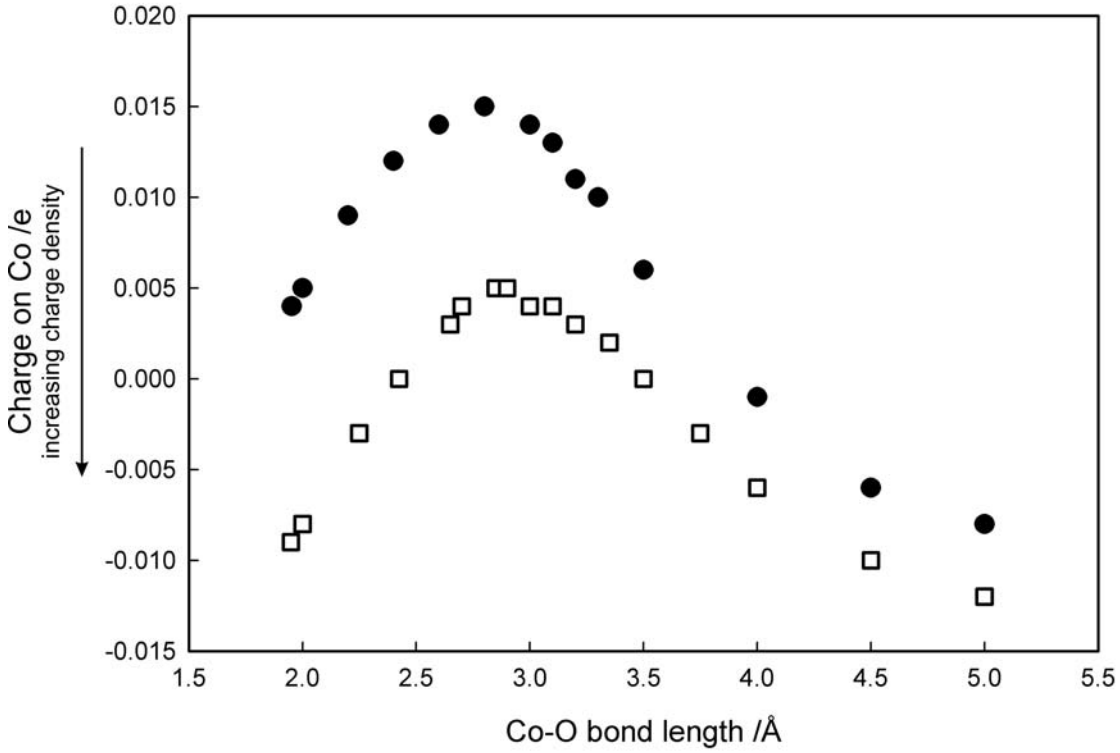

Figure S2. Dependence of the partial charge (from a MPA using semi-empirical MO calculations and the ZINDO/1 model) on cobalt in (●) H_2OCbl^+ and (□)10–Cl–H_2OCbl^+ as a function of the Co–O bond length