10.1071/CH16674_AC

Australian Journal of Chemistry 2017, 70(5), 576-580

Supplementary Material

Oxidation of cobalt(II) bispidine complexes with dioxygen

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Dedidated to Len Lindoy on occasion of his 80th birthday

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Analytical data

$[Co^{II}(L^1)Cl]CoCl_3(NCMe)$ ($C_{30}H_{32}Cl_4Co_2N_6O_5$, 816.29 g/mol). HR-ESI MS (pos, MeOH/MeCN): $[Co^{II}(L^1)OMe(MeOH)]^+$ calcd. 637.1941, obsd. 637.1951. Elemental analysis (report no. 36945): $[Co^{II}(L^1)Cl]CoCl_3(NCMe)\cdot Et_2O$ calcd C, 45.86; H 4.75; N 9.44 %; obsd C, 46.11; H 4.60; N 9.52 %.

X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Table S1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu-K_a radiation, microfocus X-ray tube, multilayer mirror optics, compounds [A]($CoCl_3$(NCMe))·solv, [B]Cl) and a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_a radiation, sealed X-ray tube, graphite monochromator, compound [C]Cl·H_2O·2MeCN) Detector frames (typically w-, occasionally j-scans, scan width 0.4...1°) were integrated by profile fitting.[1] Data were corrected for air and detector absorption, Lorentz and polarization effects[2-3] and scaled essentially by application of appropriate spherical harmonic functions.[2-6] Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling process) and augmented by a spherical correction,[5-6] or numerically (Gaussian grid).[7-8] For datasets collected with the microfocus tube(s) an illumination correction was performed as part of the numerical absorption correction.[8] The structures were solved by the charge flip procedure[9-10] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[11-13] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data the positions of some hydrogen atoms (those on the NH and OH groups and solvent water molecules) were taken from difference Fourier syntheses

and refined. Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization (acetonitrile and/or diethyl ether) was removed from the structure of [A]($CoCl_3$(NCMe))·solv with the BYPASS procedure,[14-15] as implemented in PLATON (SQUEEZE).[16-17] Partial structure factors from the solvent masks were included in the refinement as separate contributions to F_{calc}.

CCDC 1518780 - 1518782 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

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74 Table S1. Crystal data of the cobalt complexes [A]($CoCl_3$(NCMe)), [B]Cl and [C]Cl·H_2O·2MeCN.

	[A]($CoCl_3$(NCMe))·solv	[B]Cl	[C]Cl·H_2O·2MeCN
formula	$C_{30}H_{32}Cl_4Co_2N_6O_5$	$C_{22}H_{34}Cl_2CoN_4O_{10}$	$C_{32}H_{37}ClCoN_7O_9$
crystal system	monoclinic	triclinic	triclinic
space group	*I* 2	*P* −1	*P* −1
a /Å	23.3949(3)	12.6867(2)	10.418(9)
b /Å	8.04492(8)	15.1147(2)	12.006(11)
c /Å	23.0550(3)	16.2975(3)	14.066(12)
α /°	90	90.4533(13)	91.633(16)
β /°	106.8282(15)	101.4534(13)	109.991(13)
γ /°	90	110.3308(15)	92.999(15)
Volume /Å^3	4153.37(9)	2862.03(8)	1649(3)
Z	4	4	2
M_r	816.27	644.36	758.06
F_{000}	1664	1340	788
d_c /Mg×m^{-3}	1.305	1.495	1.527
μ /mm^{-1}	8.960	0.845	0.668
max., min. transmission factors	0.814, 0.250 [a]	0.973, 0.926 [a]	0.7461, 0.6621 [b]
X-radiation, λ /Å	Cu-K_α, 1.54184	Mo-K_α, 0.71073	Mo-K_α, 0.71073
data collect. temperat. /K	120(1)	120(1)	100(1)
θ range /°	3.9 to 71.0	3.3 to 29.0	2.1 to 30.7
index ranges *h*,*k*,*l*	−28 ... 28, −9 ... 9, −27 ... 28	−17 ... 16, −20 ... 20, −20 ... 21	-14 ... 14, -17 ... 17, -19 ... 20
reflections measured	66283	67110	39230
reflections unique [R_{int}]	7835 [0.0635]	13984 [0.0522]	10083 [0.0473]
reflections observed [$I \geq 2\sigma(I)$]	7543	11191	7491
data / restraints /parameters	7835 / 1 / 429	13984 / 0 / 775	10083 / 0 / 472
GooF on F^2	1.033	1.097	1.024
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0279, 0.0675	0.0526, 0.1032	0.0444, 0.1068
R indices (all data) $R(F)$, $wR(F^2)$	0.0297, 0.0685	0.0732, 0.1113	0.0697, 0.1178
largest residual peaks /e×Å^{-3}	0.044, 0.342, −0.215	0.079, 0.589, −0.320	0.082, 0.699, -0.565

75 [a] numerical absorption correction; [b] empirical absorption correction

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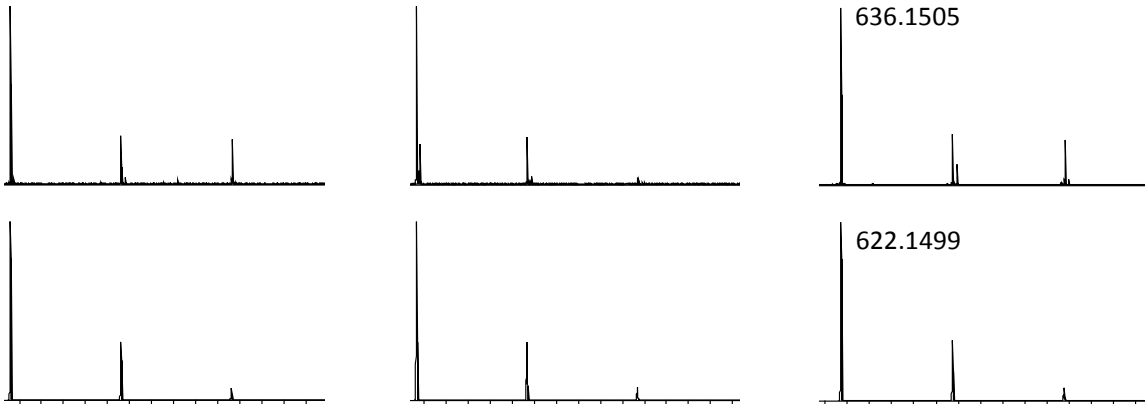

Figure S1. Experimental (top) and calculated (bottom) isotopic patterns from the reaction of A (2 mM in MeOH) with O_2 in MeOH (HR-ESI^+ MS).

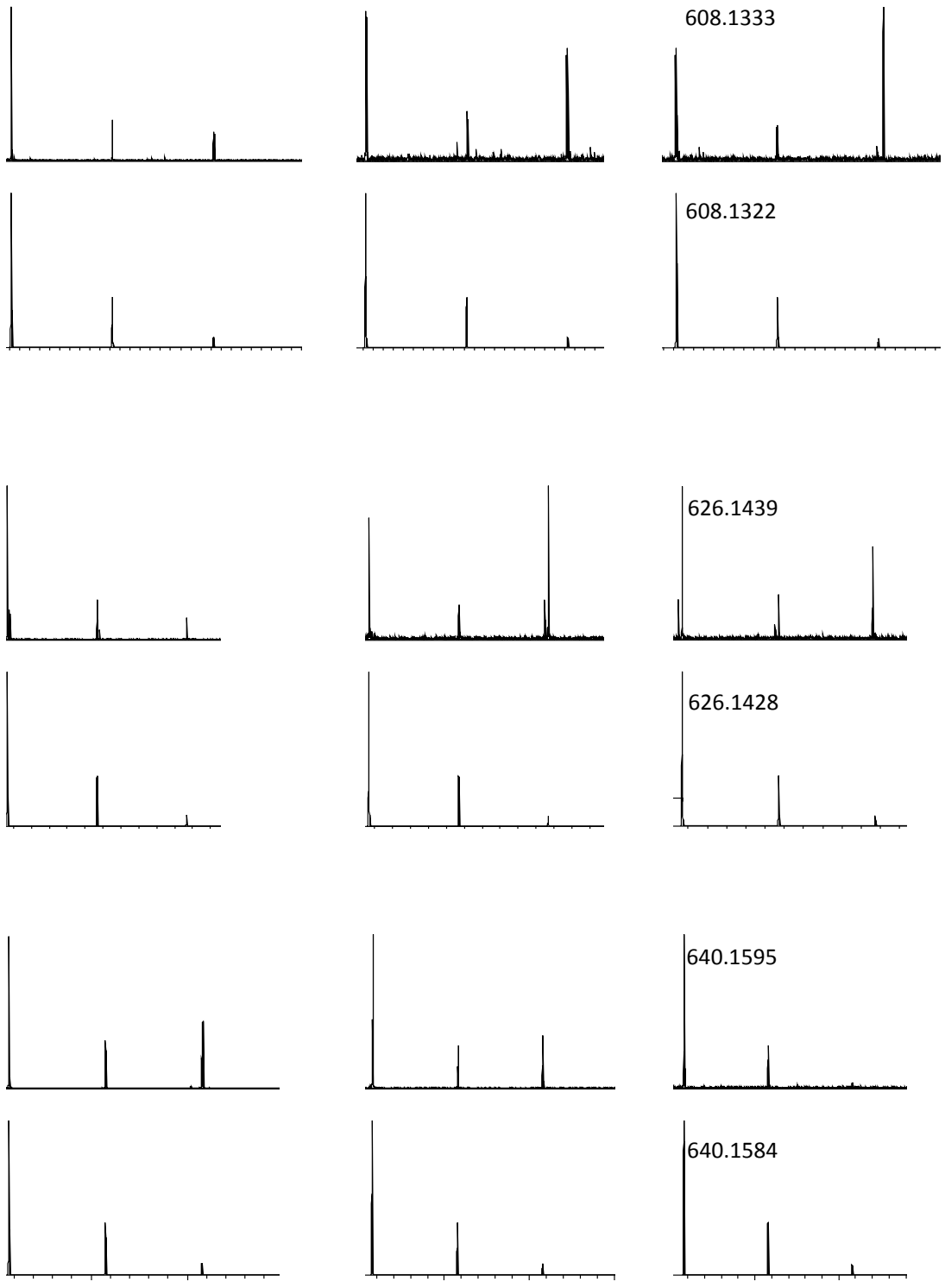

Figure S2. Experimental (top) and calculated (bottom) isotopic patterns from the reaction of A (2 mM in MeOH) with mixture of $^{16}O_2$ / $^{18}O_2$ in MeOH (HR-ESI$^+$ MS).

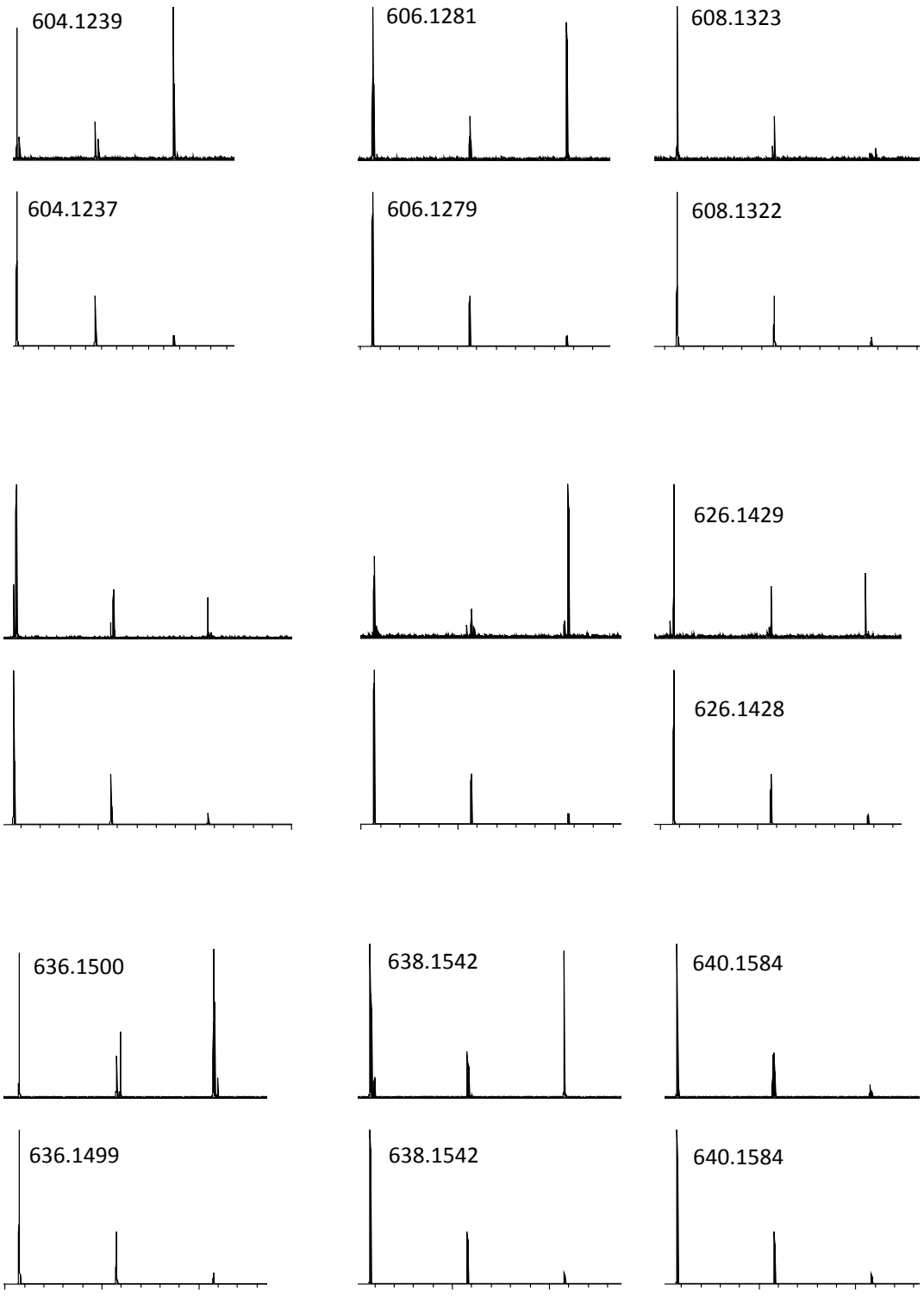

Figure S3. Experimental (top) and calculated (bottom) isotopic patterns from the reaction of A (2 mM in MeOH) with pure $^{18}O_2$ in MeOH (HR-ESI$^+$ MS).