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Synthesis, structure and catalytic activity of low-spin dicyano iron(III) complexes of N, N'-bis(quinolyl)malonamide derivatives $\stackrel{\stackrel{_{\scriptstyle \leftarrow}}{\sim}}{}$

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Abstract

Two low-spin Fe(III) dicyano-dicarboxamido complexes have been prepared from N, N'-bis(8-quinolyl)malonamide derivatives. Crystal structures show that the four nitrogen donors available to complex the metal are arranged in the equatorial plane with the two cyanides *trans* to each other in the axial positions when the malonyl moiety is disubstituted. In contrast, the unsubstituted malonyl results in only three nitrogens in the equatorial plane with the fourth in an apical position and the two cyanides occupying *cis* sites, one equatorial and the other axial. NMR analyses show that the solid state structure of both complexes is retained in solution. Both types of configurational complexes catalyze cyclic olefin oxidations with H₂O₂ but only the *cis*-dicyano complex catalyzes stilbene oxidation with formation of epoxides, diols and benzaldehyde. © 2004 Elsevier B.V. All rights reserved.

Keywords: N, N'-bis(8-quinolyl)malonamide; Iron(III) complex; Oxidation; Stilbene

1. Introduction

There has been growing interest in developing mimics of mononuclear non-heme iron proteins capable of catalyzing alkane hydroxylation [1], olefin epoxidation, and more recently, olefin *cis*-dihydroxylation [2]. Most of the complexes reported so far which catalyze *cis* diols formation contain amine and pyridine nitrogen donors, such as tris-(pyridylmethyl)amine ligands, which stabilize the Fe(II) state [2]. Introduction of one or more carboxamido nitrogens in the coordination sphere is known to increase the stability of Fe(III) [3a] and affords mononuclear Fe(III) complexes which exhibit significant oxidative activity with peroxides such as H_2O_2 or tBuOOH [3b– 3d,4,5]. Complexes containing dianionic bis(amidate) ligands, usually derived from picolinic acid, afford six-coordinate complexes with an equatorial N4 core and two apical exogenous ligands [3c,4,6,7]. We report here the syntheses, structures and reactivities of new dicyano Fe(III) complexes derived from N, N'-8-quinolylmalonamide derivatives (Fig. 1). The spatial configuration of the bis-carboxamido ligands depends on whether the methylene position of the malonamide is unsubstituted or disubstituted, yielding six-coordinate complexes with two *cis* or *trans* cyanides which exhibit different oxidative activity with H₂O₂ toward cyclic olefins and stilbene.

2. Experimental

2.1. Physical measurements

UV–Vis spectra were recorded on a Safas UV mc^2 spectrophotometer. X-band EPR spectrum was

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recorded on an ALEXIS spectrometer operating at a 9.45 GHz microwave frequency (100 kHz modulation frequency, 1 mT modulation amplitude, 20 mW microwave power). ¹H NMR spectra were recorded at 300 K on a Bruker ARX-250 spectrometer. Chemical shifts are reported in ppm downfield from TMS. Infrared spectra were obtained as KBr pellets or directly from the solid compounds (neat) with a Perkin-Elmer Spectrum One FT-IR spectrometer. Cyclic voltammetry experiments were performed with a potentiostat Radiometer PJT-1 controlled by an interface Radiometer IMT-1 using solutions containing 0.1 M Bu₄NBF₄ as supporting electrolyte. The three electrode systems consisted of an NaCl saturated calomel electrode (SCE) as reference, a platinum auxiliary electrode and a glassy carbon working electrode. Ferrocene was used as an internal standard ($E_{1/2}(Fc^{0/+})$ in DMF, 50 mV/s, +508 mV at 20 °C and +515 mV at -40 °C). Elemental analyses were carried out by the microanalysis service at Paris VI University.

2.2. Synthesis of the ligands

N, N'-Bis(8-quinolyl)malonamide BQMH₂: under argon malonyl chloride (972 µL, 9.5 mmol) was added to a solution of 8-aminoquinoline (3.17 g, 22 mmol) and triethyl amine (1.5 mL,10 mmol) in 100 mL of CH₂Cl₂. After addition of another 1.5 mL triethyl amine, the mixture was stirred for 12 h. CH₂Cl₂ was added until all precipitated condensation products were dissolved, then the solution was washed three times with water and then with saturated NaHCO₃. After drying over Na_2SO_4 , the solvent was removed and the product was recrystallized from CH_2Cl_2 (m = 1.32 g, yield 39%). Anal. Calc. for C₂₁H₁₆N₄O₂: C, 70.78; H, 4.49; N, 15.73. Found: C, 70.60; H, 4.66; N, 15.68%. ¹H NMR (CDCl₃, ppm): 10.78 (s, 2H, NH), 8.89 (dd, J = 1.6, 4.4 Hz, 2H), 8.83 (dd, J = 3.6, 5.6 Hz, 2H), 8.16 (dd, J = 1.6, 8.4 Hz, 2H),7.55 (dd, J = 3.6, 5.6 Hz, 2H), 7.46 (dd, J = 4.4, 8.4 Hz, 2H), 3.87 (s, 2H). IR (neat, cm⁻¹): 3279 (w, $v_{\rm NH}$), 1646 $(m, v_{\rm CO}).$

The substituted ligand **1b** was synthesized according to Hirose et al. [8b], but the saponification of the ma-

lonic ester was carried out by the procedure reported by Maslak et al. [9].

2.3. Synthesis of complexes 2a and 2b

In a typical experiment, performed under argon, 100 mg FeCl₂ \cdot 4H₂O (0.5 mmol, 1 equiv) was dissolved in 5 mL DMF and combined with 1 equiv of the corresponding ligand in 20 mL DMF. Upon addition of $200 \,\mu\text{L NEt}_3$ (3 equiv), the solution turned dark red. The mixture was cooled to -30 °C and 0.47 g Et₄NCN (6 equiv) in 10 mL DMF was added (color turned into intense green), followed by 200 mg of the oxidizing agent $C_6H_4FN_2PF_6$ [10] (1.5 equiv) in 5 ml DMF. The final dark brown solution was allowed to warm to r.t. and the solvent was removed in vacuum. The crude product was dissolved in 25 mL MeOH and the remaining white residue (unconverted ligand) was filtered off before the green complex was precipitated by addition of ether. (2a: 265 mg, 2b: 347 mg, yield 2a, 2b: 90%). The complexes were further additionally purified over a Sephadex LH-20 resin (Amersham Biosciences).

Analytical data and spectroscopic properties of the complexes: [Fe(BQM)(CN)₂]Et₄N (2a): Anal. Calc. for C₃₄H₅₀N₇O₇Fe (2a · 2H₂O · 3CH₃OH): C, 56.53; H, 6.95; N, 13.53. Found: C, 56.04; H, 6.94; N, 13.44%. ¹H NMR (CD₂Cl₂, ppm): 17.7, 11.9, 10.4, 9.2, 7.0, 5.0, 1.2, -2.8, -7.3, -11.6, -20.8, -25.3, -29.5 (1H each). Selected IR frequencies (KBr, cm⁻¹): 2116 (w, v_{CN}), 1616 (*m*, v_{CO}). Electronic absorption λ_{max} nm (ϵ , M⁻¹ cm⁻¹): CH_2Cl_2 , 250 (2.0 × 10⁴), 368 (3.2 × 10³), 440 (2.5 × 10³), 696 (7.1 × 10²). EPR (DMF, 5% H₂O): $g_x = 2.52$, $g_y = 2.19, g_z = 1.82. E_{1/2}[Fe(BQM)(CN)_2]^{2-/-}(versus$ SCE) (DMF, Bu₄NBF₄, 10 equiv Et₄NCN, 20 °C): -605 mV ($\Delta E = 90$ mV). [Fe(BenzBQM)(CN)₂]Et₄N (**2b**): Anal. Calc. for $C_{47}H_{49}N_8O_2Fe$ (**2b** · CH₃CN): C, 69.37; H, 6.07; N, 13.77. Found: C, 68.92; H, 6.07; N, 13.76%. ¹H NMR (DMSO-d6, ppm): 10.4 (2H), 7.5–6.9 (10H, ar), 5.4 (2H), 1.3 (2H), -0.5 (4H, CH₂), -8.2 (2H), -13 (2H), -26.5 (2H). Selected IR frequencies (KBr, cm⁻¹): 2112 (w, v_{CN}), 1607 (m, v_{CO}). Electronic absorption λ_{max} nm (ϵ , M⁻¹ cm⁻¹): MeOH, 254 (2.7 × 10⁴), 362 (4.2×10^3) , 440 (5.0×10^3) , 702 (9.3×10^2) . EPR (DMF, 5% H₂O): $g_x = 2.56$, $g_y = 2.15$, $g_z = 1.82$. E_{1/2}[Fe(BenzBQM)(CN)₂]^{2-/-}(versus SCE) (DMF, Bu₄NBF₄, 10 equiv Et₄NCN, 20 °C): $-645 \text{ mV} (\Delta E = 110 \text{ mV}).$

2.4. X-ray crystallography

Crystal data and data collection parameters for complexes **2a** and **2b** are summarized in Table 1, while selected bond angles and distances are listed in Table 2.

2.4.1. X-ray crystallography of 2a

Data were measured at 108 K on a MAR345 image plate detector at beamline X7B at the Brookhaven

 $Å^{-3}$.

Table 1 Crystal data and structure refinement

$C_{31}H_{34}N_7O_2Fe$,	$C_{47}H_{49}N_8O_2Fe$ (2b)
$2(H_2O)(2a)$	
methylene chloride/	acetonitrile/
toluene	diethylether
628.53	813.79
C_2/c	Pbc_21
8	4
108	180
33.778 (8)	11.114 (1)
13.747 (1)	19.172 (3)
14.288 (4)	19.384 (3)
90	90
92.69 (1)	90
90	90
6627.3 (2)	4130.8 (8)
dark blue	dark green
irregular cube	parallelepiped
1.260	1.309
0.08 imes 0.07 imes 0.07	$0.10\times0.28\ \times0.08$
0.499	0.415
0.9376	0.71073
2.11-30.94	3.67-30.32
45 433/4065	35 189/11 499
3774	8180
280	579
369	526
0.051 0.140	0.040.0.000
0.051; 0.148	0.049; 0.086
0.057; 0.163	0.077; 0.0956
1.096	0.942
	$\begin{array}{c} C_{31}H_{34}N_7O_2Fe,\\ 2(H_2O) \ (2a)\\ methylene chloride/\\toluene\\ 628.53\\ C_2/c\\ 8\\ 108\\ 33.778\ (8)\\ 13.747\ (1)\\ 14.288\ (4)\\ 90\\ 92.69\ (1)\\ 90\\ 6627.3\ (2)\\ dark\ blue\\ irregular\ cube\\ 1.260\\ 0.08\times 0.07\times 0.07\\ 0.499\\ 0.9376\\ 2.11-30.94\\ 45\ 433/4065\\ 3774\\ 389\\ 0.051;\ 0.148\\ 0.057;\ 0.163\\ 1.096\\ \end{array}$

Table 2

Selected	bond	angles	(°)	and	distances	(A)	for	complexes
[Fe(BQM)(CN) ₂]Et ₄ N (2:	a) an	d [Fe((BenzBQM)	(CN)	$_2]Et_4N$	N (2b)

	2a	2b
Fe–N1	1.974(3)	1.982(2)
Fe–N2	1.958(2)	1.916(2)
Fe-N3	1.940(3)	1.941(2)
Fe–N4	2.032 (3)	2.000(3)
Fe-C22	1.954(4)	1.968(3)
Fe-C23	1.930(4)	1.975(3)
C22–N5	1.152(4)	1.152(3)
C23–N6	1.147(4)	1.145(3)
N2–Fe–N4	100.89(10)	173,77(9)
N1-Fe-N4	90.05(12)	100.54(8)
C23-Fe-C22	83.71(13)	171.79(9)
C22-Fe-N2	171.88(12)	95.25(10)
C23-Fe-N4	168.97(12)	84.64(9)

National Synchrotron Light Source. The data were scaled and merged using Denzo/Scalepack [11]. The structure was solved with SIR92 [12] and refined on F_2 (SHELXTL Version 5) [13]. The lattice contains an extremely disordered molecule of solvation, which was unmodelable. The program SQUEEZE in the PLATON

2.4.2. X-ray crystallography of 2b

Intensity data were collected on a Xcalibur system using ω -scan technique ($\Delta \omega = 1^{\circ}$, 460 frames, the exposure time depending on the intensity of the frame) [15]. The structure was solved by direct methods using SHELXS-97 [16] and refined by full matrix least-squares methods on F_2 [17]. Non-hydrogen atoms were refined with anisotropical thermal parameters. Hydrogen atoms were calculated for idealized geometries and refined as riding models with isotropic parameters constrained to be 1.2 times the U_{eq} of the carrier atom. The residual density in the final difference Fourier does not show any feature above 0.473 e Å⁻³ and below -0.439 e Å⁻³. ORTEPII was used to produce molecular graphics [18].

2.5. Catalytic oxidation reactions

Oxidation reactions with complexes 2a and 2b were carried out in the presence of air under atmospheric pressure. For cyclooctene and cyclohexene, the complex (1 µmol) and the substrate (800 µmol) were dissolved in 1 mL acetonitrile and the mixture was stirred at 65 °C. Stepwise addition of H₂O₂ was performed as mentioned

Table 3

Results of olefins oxidation with complexes 2a and 2b in acetonitrile at 65 °C

Substrate/products ^a	Equivalents of products relative to complex		
	Fe(BQM)(CN) ₂ (2a)	Fe(BenzBQM)(CN) ₂ (2b)	
Cyclooctene ^{b,c}			
Cyclooctene oxide	40 (19) ^d	42 (22) ^d	
Cyclooctene diol	6 (2) ^d	7 (2) ^d	
Cyclohexene ^{c,e}			
Cyclohexene oxide	9	7	
2-cyclohexene-1-ol	39	37	
2-cyclohexene-1-one	41	38	
<i>cis-stilbene</i> ^{f,g}			
cis-stilbene oxide	0.5	0.1	
trans-stilbene oxide	4.3	0.1	
cis-silbene diol	1.3	0.1	
trans-stilbene diol	0.9	not detected	
Benzaldehyde	16.0	1.9	

^a Products were identified by comparison with authentic samples.

^bAddition of 5×60 equiv H₂O₂ in intervals of 1 h.

^c Yields were determined after 8 h by gas chromatography.

^d Values in brackets were obtained with 0.5 equiv of catalyst.

^e Addition of 12×25 equiv H₂O₂ every 30 min.

^fAddition of 8×20 equiv H₂O₂ every 30 min.

^g Yields were determined after 5 h by NMR integration of characteristic protons. Reactions were carried out in acetonitrile-d₃.

in Table 3. After 8 h, 20 equiv of acetophenone were added as an internal standard and the amounts of oxidation products were determined by G.C. For stilbene, 1 mL of acetonitrile- d_3 was used as a solvent and (due to the reduced solubility) 0.5 µmol of catalyst was employed with 200 equiv of the substrate. After 5 h, product yields were determined by NMR integration of characteristic protons compared to the methyl group of acetophenone (standard). All reactions were run at least in triplicate and the reported data represent the average values.

3. Results and discussion

N, N'-Bis(8-quinolyl)malonamide, **1a**, was readily synthesized by condensing 8-aminoquinoline with malonyl dichloride. The disubstituted derivative **1b**, which has been previously reported and shown to complex divalent metals [8], was synthesized as described in [8b,9]. Fe(II) was readily incorporated into all two ligands with FeCl₂ · 4H₂O in the presence of the soft base Et₃N. Addition of Et₄NCN, followed by oxidation of the resulting dicyano iron(II) complexes with the oneelectron oxidizing agent 4-fluorobenzenediazonium hexafluorophosphate [10], afforded in good yields the two iron(III) complexes [Fe(BQM)(CN)₂]Et₄N, **2a** and [Fe(BenzBQM)(CN)₂]Et₄N, **2b**. The structures of complexes **2a** and **2b** have been determined by X-ray crystallography.

Figs. 2 and 3 show the structures of **2a** and **2b**, respectively, and selected bond angles and distances are listed in Table 2. The two structures reveal an octahedral environment for the Fe(III) centers. However, while the four nitrogen donors N1–N4 in **2b** lie in the equatorial plane with the two cyanides situated axially and *trans* to each other (Fig. 3), in **2a** only three nitrogens, N1, N2, N3, lie in the equatorial plane with the fourth, N4, in an



Fig. 2. Thermal ellipsoid plot (50% probability level) of the anion of **2a**. H atoms are omitted for clarity.



Fig. 3. Thermal ellipsoid plot (50% probability level) of the anion of **2b**. H atoms are omitted for clarity.

apical position with the two cyanides occupying *cis* sites, one equatorial (C22–N5) and the other axial (C23–N6), see Fig. 2. The steric constraints imposed by the introduction of two substituents at C11 of the malonyl fragment in **2b** thus favor its planar configuration and the resulting equatorial arrangement of all four donor nitrogens. Note that the distances from the Fe to the cyanides are essentially equivalent in **2b**, 1.972(3) Å, but are shorter and inequivalent in **2a**, 1.954(4) Å and 1.930(4) Å, reflecting the stronger donor character of the amidate N2 relative to that of the pyridine N4.

Both complexes have been characterized in solution. They are reversibly reduced in DMF at 20 °C, in the presence of an excess of Et₄NCN (E_{1/2} -605 and -645 mV versus SCE for 2a and 2b (Fig. 4(a)), respectively). Without added cyanide as shown in Fig. 4(b), the reduction of the *trans* complex at -700 mV is followed by two reoxidation waves at -590 and -100 mV typical of an ECE mechanism in which one or both cyanides are lost. The loss of cyanide(s) after the reduction thus reflects a low binding affinity of cyanide for the Fe(II) state. The wave at -100 mV may be attributed to the one-electron oxidation of a $[Fe(BenzBQM)(DMF)_2]^{2-1}$ species having two loosely bound DMF molecules. However, the binding affinity of cyanide to the iron(II) increases as the temperature decreases. The reduction became completely reversible at -40 °C and the second oxidation wave disappeared. The same result was obtained with the *cis* complex (data not shown). The Xband EPR spectra of the Fe(III) dicyano in frozen DMF/H₂O 5% solution at 10 K are typical of a low-spin iron(III) state and display a rhombic signal with g values similar to those reported for the dicyano picolinic derivatives [6,7c]. Their NMR spectra shown in Fig. 5 spread over the range -30 to +20 ppm, but are very different as expected if their solid state structures are



Fig. 4. Cyclic voltammetry of *trans*-**2b** (DMF/Bu₄NBF₄): (a) with Et₄NCN in excess; (b) at different temperatures from 20 to -40 °C.

retained in solution. The spectrum of **2b** (Fig. 5(b)) shows six resonances, with an integration ratio of 2H each, assigned to the 12 quinolyl protons showing that the two quinolyl rings are equivalent. These resonances are calibrated in reference to the signal attributed to the four benzylic protons. In contrast, the spectrum of **2a** (Fig. 5(a)) displays 13 signals with an integration ratio of 1H each. This result supports the absence of any symmetry in the solution structure of **2a** as in the solid state and consequently that the two quinolyl rings are unequivalent. Indeed, 14 resonances were expected, since the two malonyl protons are also unequivalent, however only 13 resonances were observed. The last one, which is missing, is probably located under the signals attributed to the Et₄N⁺ counter cation.

Despite their different configurations, the two complexes exhibit similar UV–Vis spectra (see Section 2) as



Fig. 5. NMR spectra of *cis*-**2a** (CH₂Cl₂-d₂) and *trans*-**2b** (DMSO-d₆) at 250 MHz.

well as comparable v_{CN} stretching frequencies, 2116 and 2112 cm^{-1} for **2a** and **2b**, respectively. Moreover, the IR spectrum of the cis complex shows only one v_{CN} stretching frequency. A similar observation has been reported for other cis-dicyano complexes such as cisdicyano-bis(1,10-phenanthroline)iron(II) [19] and cisdicyano-bis(2,2'-bipyridine)iron(III) perchlorate [20]. When comparing the structures of **2a** and **2b**, both C–N bond distances in the two complexes fall effectively within a narrow range of 1.145 (3) to 1.152 (3) A (Table 2). This could explain the similar v_{CN} values for **2a** and 2b and the presence of only one cyanide vibration for 2a. In contrast the Fe-CN bond lengths are significantly shorter in 2a than in 2b (Δ (2a-2b, Fe-C22) = -0.014 A and $\Delta(2a-2b, Fe-C23) = -0.045$ Å, Table 2). This should only induce differences in the lower-frequency bands (v_{Fe-CN}) in the region 600–350 cm⁻¹ that we cannot explore with a sufficient accuracy under our IR spectrum recording conditions. The v_{CN} of cyano complexes is known to be governed by (1) the electronegativity, (2) the oxidation state of the metal and (3) the number of cyanide ligands [21]. Despite their different structures, the properties of 2a and 2b in solution are very similar, except for the NMR. The electronic properties of the metal center are identical in 2a and 2b in agreement with the very similar redox potentials of these complexes determined by electrochemistry. Their EPR spectra display very similar g values, which are also

within the range of those obtained for other dicyano complexes containing bis-amidate ligands derived from picolinic acids [6,7a]. CN^- acts as a strong σ donor and a poor π acceptor and so is not very sensitive to metalligand back donation, which should be different whether the N4 macrocycle adopts a helical or planar configuration. It seems very likely that the strong effect of the two cyanides prevails over the effect of the N4 ligand, and therefore the electronic properties are not very sensitive to the difference of configuration between **2a** and **2b**.

The different structures of the two related Fe(III) complexes with two cis or trans exogenous ligands prompted us to test the reactivity of 2a and 2b toward olefin oxidation in CH₃CN with H₂O₂ as an oxidant. Recently, it has been pointed out that the main structural feature responsible for cis-dihydroxylation of olefins versus epoxidation was the presence of two labile cis sites [2a]. Cyanide is usually proposed to be tightly bound to the metal center, but while complexes 2a and 2b were poorly active at room temperature, they display a significant reactivity at 65 °C. Increasing the temperature probably allows the exchange of one or two cyanides with the solvent and the further binding of H_2O_2 . The best conditions for the catalytic oxidations were the stepwise addition of the oxidant over time, which limited the disproportionation of H_2O_2 . As shown in Table 3, both complexes exhibit a similar reactivity toward cyclooctene and cyclohexene and favor the formation of cyclooctene oxides versus diols (ratio \sim 6:1), and mainly allylic oxidation of cyclohexene. No conversion was observed in the absence of the catalysts. Reducing the catalyst concentration produced a similar decrease of the conversion yields of cyclooctene oxidation products (Table 3 and footnote d). In contrast, while 2b was quite inactive toward stilbene oxidation, 2a was able to convert 23 (± 2) equivalents of the substrate (relative to the catalyst). Besides the formation of benzaldehyde, 2a promotes the formation of both stilbene oxides (cis:trans isomers 1:9) and diols in a 7:3 ratio. (The stilbene oxides were stable under the experimental conditions.) Interestingly, a similar product distribution has been previously described by Meunier and co-worker for stilbene oxidation mediated by iron-bleomycin and KHSO₅ [22].

4. Conclusion

The compounds described thus represent a new class of complexes with the same type of nitrogen donors, whose coordination geometry to the metal center is defined by a substitution on the ligand framework. As catalysts, they yield a spectrum of olefin oxidation products with H_2O_2 that include epoxides, ketones, aldehydes, alcohols and diols with only the cis dicyano derivative capable of selectively oxidizing the aromatic stilbene. While the catalytic reaction is significant, these catalysts are only poorly active. To facilitate the reaction of these complexes with the oxidant, we first intend to replace the cyanides by more labile exogenous ligands. This should allow: (i) to work at room temperature, (ii) to limit the side reaction of H_2O_2 disproportionation, and (iii) to increase the difference in the physicochemical properties according to the configuration of the complexes. Furthermore, the electronic properties of the macrocycle will be modified by introducing substituents on the quinolyl ring. These modifications should allow mechanistic investigations for understanding the different chemical reactivities of the cis and trans complexes toward substrates.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 182345 for compound [Fe(BenzBQM)(CN)₂]Et₄N and CCDC No. 211027 for compound [Fe(BQM)(CN)₂]Et₄N. Copies of these informations can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk, or http://ccdc.cam.ac.uk].

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