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The reaction of nitro-1,2-diaminobenzenes with the $[ReO]^{3+}$ core: isolation of oxo-free rhenium(V) complexes

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Abstract

The reaction of 2 equiv. of 3-nitro-1,2-diaminobenzene (H_2L^1) with *trans*-$ReOCl_3(PPh_3)_2$ in ethanol gave the oxo-free rhenium(V) complex $[ReCl(PPh_3)(L^1)_2]$ (**1**) in good yield. IR, ^1H NMR and X-ray crystallographic results indicate that the diamine ligand L^1 coordinates in a dianionic bidentate diamido form to the metal, and that the complex has the unusual skew-trapezoidal bipyramidal geometry. With 4-nitro-1,2-diaminobenzene (H_2L^2) as ligand the complex $[Re(L^2)Cl_3(PPh_3)_2]$ (**2**) was characterized, in which L^2 coordinates in a dianionic monodentate imido form through one nitrogen only. Crystal data for **1**·EtOH: $C_{32}H_{31}ClN_6O_5PRe$, monoclinic $P2_1/c$, $a = 14.937(11)$, $b = 15.017(8)$, $c = 15.394(12)$ Å, $\beta = 112.12(6)°$, $V = 3198.7(38)$ Å^3, $Z = 4$, $D_{calc} = 1.728$ g cm^{-3}, structure solution and refinement based on 3151 reflections converged at $R = 0.0807$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Rhenium complexes; Oxo-free complexes; Nitro-diamine complexes

1. Introduction

The success of therapeutic rhenium radiopharmaceuticals in the palliation of osseous metastases in cancer patients [1] has rekindled interest in the coordination chemistry of this metal. These research efforts concentrate mainly on the V oxidation state, since it is easily obtained from the reduction of perrhenate and easily stabilized by a large variety of ligands [2]. However, the most distinctive feature of Re(V) chemistry is the existence of a large number of stable complexes in which the metal forms multiple bonds to oxygen, nitrogen or sulfur [3]. These complexes are mostly octahedral and contain one of the $[ReO]^{3+}$, $[ReO_2]^{+}$, $[Re_2O_3]^{4+}$, $[Re{\equiv}N]^{2+}$, $[Re{=}NR]^{3+}$ or $[Re{=}S]^{3+}$ moieties. These multiply bonded donor atoms severely restrict the structure, geometry, configuration, reactivity and magnetic properties of Re(V) complexes.

Complexes of Re(V) which lack such multiple bonds are rare and unusual. The few examples in the literature ($ReH_5(PPh_3)_2(py)$ and its derivatives, $ReCl_5$, $[ReX_4(diars)_2]^{+}$ and $[Re(HNC_6H_4S)_3]^{-}$) [4] were synthesized by either the reduction of Re(VI) and Re(VII) or the oxidation of Re(III) and Re(IV) species under extreme conditions. The only sample that could be found where the synthesis was via the ligand substitution of a rhenium(V) starting complex containing one of the multiply bonded moieties mentioned above, is $[ReH_5(PR_3)_3]$ [5]. It was made by treating *trans*-$[ReOCl_3(PPh_3)_2]$ (or $ReCl_3(PR_3)_3$) with $LiAlH_4$ or $NaBH_4$ in thf.

This paper describes the products of the reactions of 3-nitro-1,2-diaminobenzene (H_2L^1) and 4-nitro-1,2-diaminobenzene (H_2L^2) (see Scheme 1) with *trans*-$ReOCl_3(PPh_3)_2$ in ethanol. With H_2L^1 the oxo-free rhenium(V) complex $[ReCl(PPh_3)(L^1)_2]$ was isolated, in which L^1 acts as a bidentate dianionic diamido chelate. With H_2L^2 the imido rhenium(V) complex $[Re(L^2)Cl_3(PPh_3)_2]$ was formed, with L^2 coordinated in a dianionic monodentate mode.

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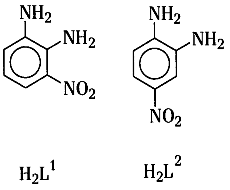


Scheme 1.

We have previously reported the products isolated from the reactions of the aromatic diamines 1,2-diaminobenzene, 2,3-diaminophenol and 2,3-diaminotoluene ($H_2N{-}R{-}NH_2$) with *trans*-$ReOCl_3(PPh_3)_2$ in ethanol. In all these cases *trans*-[$Re(N{-}R{-}NH_2)Cl_3(PPh_3)_2$] was isolated, in which the diamine ligands coordinate to rhenium(V) in the dianionic monodentate imido form [6].

2. Experimental

2.1. Reagents

trans-$ReOCl_3(PPh_3)_2$ was synthesized by a published procedure [7]. Solvents were reagent grade, and were purified, dried and deoxygenated before use. All other reagents were obtained commercially (Aldrich), and their purity was checked by ^1H NMR and melting point. All reactions were performed under a nitrogen atmosphere, using standard techniques.

2.2. Synthesis

2.2.1. [$ReCl(PPh_3)(L^1)_2$] (**1**)

A mixture of 106 mg (127 μmol) of *trans*-$ReOCl_3(PPh_3)_2$ and 39 mg (255 μmol) of H_2L^1 in 30 cm^3 of ethanol was heated under reflux conditions for 3 h. After cooling the solution to room temperature (r.t.), a dark reddish–brown crystalline precipitate was removed by filtration, washed with ethanol and diethyl ether, and dried under vacuum. Recrystallization was from acetone; yield 65.5 mg (62%), m.p. > 300°C. *Anal.* Calc. for $C_{30}H_{25}ClN_6O_4PRe$: C, 45.83; H, 3.21; N, 10.69. Found: C, 45.99; H, 3.24; N, 10.78%. IR (KBr): ν(NH) 3332(m), 3284(m); $\nu_s(NO_2)$ 1339(s); ν(Re–Cl) 301(m). ^1H NMR (294 K) ppm: 13.59 (s, 2H, N^2H); 13.21 (s, 2H, N^1H); 7.69 (d, 2H, H^4); 7.64 (d, 2H, H^6); 7.37–7.49 (m, 9H, P*Ph*$_3$); 7.12 (m, 6H, P*Ph*$_3$); 6.96 (t, 2H, H^5). UV–Vis: 482 (5900), 380 (14 700), 329 (15 400), 228 (56 200).

2.2.2. [$Re(L^2)Cl_3(PPh_3)_2$] (**2**)

To 109 mg (130 μmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 20 cm^3 of ethanol was added 40 mg (261 μmol) of H_2L^2, and the resultant solution was heated under reflux conditions for 2 h. After cooling to r.t., the solution was filtered to give an orange precipitate, which was washed with ethanol and diethyl ether, and dried. Recrystallization from acetonitrile gave orange prisms; yield 66 mg (52%), m.p. 159°C. *Anal.* Calc. for $C_{42}H_{35}Cl_3N_3O_2P_2Re$: C, 52.10; H, 3.64; N, 4.34. Found: C, 51.81; H, 3.66; N, 4.35%. IR (KBr): $\nu(NH_2)$ 3390(m), 3195(m); $\delta(NH_2)$ 1631(m); $\nu_s(NO_2)$ 1330(vs); ν(Re≡N–) 1092(m); ν(Re–Cl) 312(m), 295(m). ^1H NMR (294 K) ppm: 8.10 (d, 1H, H^5); 7.91 (m, 14H, NH_2, PPh$_3$); 7.44 (m, 18H, P*Ph*$_3$); 6.86 (s, 1H, H^3); 6.38 (d, 1H, H^6). UV–Vis: 458 (8800), 363 (11 000), 332 (10 400), 259 (42 100).

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{32}H_{31}ClN_6O_5PRe$
Formula weight	832.25
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	14.937(11)
b (Å)	15.017(8)
c (Å)	15.394(12)
α (°)	90
β (°)	112.12(6)
γ (°)	90
Volume (Å^3),	3199(4),
Z	4
D_{calc} (Mg m^{-3})	1.728
Absorption coefficient (mm^{-1})	3.984
$F(000)$	1648
Crystal size (mm)	0.10 × 0.08 × 0.05
θ Range for data collection (°)	2.68–20.05
Limiting indices	$0 \leq h \leq 14$, $0 \leq k \leq 14$, $-14 \leq l \leq 13$
Reflections collected	3151
Independent reflections	3010 ($R_{int} = 0.0998$)
Observed reflections ($I > 2\sigma(I)$)	1739
Absorption correction	No
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3008/0/221
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0807$, $wR_2 = 0.1917$
R indices (all data)	$R_1 = 0.1466$, $wR_2 = 0.2519$
Extinction coefficient	0.0000(4)
Largest difference peak and hole (e Å^{-3})	0.989 and −0.833

2.3. X-ray data collection, structure solution and refinement of **1**

Crystals of the formulation [$ReCl(PPh_3)(L^1)_2$]·EtOH were obtained from a 1:1 mixture of ethanol and dichloromethane solvents. The crystal data and details of data collection are given in Table 1. The crystal data and intensities were measured on a Nicolet Siemens R3m/V four-circle diffractometer (Mo Kα, $\lambda = 0.71073$ Å), using the $\omega{-}2\theta$ technique. Unfortunately, all the crystals were of a small size and the only remotely suitable sample for a single-crystal structure determination was substandard. Poor quality was quickly manifested in the broad scan widths during early search routines on the diffractometer. In addition, the diffracting ability of the sample fell off rapidly with increasing Bragg angle and the data collection was restricted to $2\theta = 40°$. Because of this, much of the higher angle data collected were weak and bore negative intensities. As a consequence, refinement of the crystal structure was not satisfactory, and moreover, it was hampered by the disorder of the ethanol molecule. The latter was found to be severely disordered into a number of partially occupied sites, but attempts to model the disorder did not produce a reliable structure, and so refinement was completed without any disorder model yielding passable residuals. Refinement on F^2 (anisotropy only to the three heavy atoms) converged rather smoothly to the fractional atomic coordinates. The structure was solved by Patterson methods using SHELXTL/PC [8] and refined by the full-matrix least-squares method using the SHELXL-93 [9] package.

The relevant bond lengths and angles are listed in Table 2. Due to the fact that the crystals were substandard and that the refinement was not satisfactory with a relatively high value for the R indices, only the bond lengths and angles in the coordination sphere around the rhenium are given, since the bond lengths and angles in the ligands L^1 and PPh_3 would be of very little chemical significance. The structural analysis did however attain its objective by providing proof of the oxidation state of rhenium and the overall stereochemistry of the complex.

2.4. Physical measurements

The scientific instrumentation used in this study is the same as reported elsewhere [10]. IR spectra were obtained in KBr discs and ^1H NMR spectra were run in $(CD_3)_2SO$. Electronic spectra were all obtained in dichloromethane, and data are given as λ_{max} with extinction coefficients (in units $M^{-1}\,cm^{-1}$) in parentheses. Elemental analyses for carbon, hydrogen and nitrogen were carried out by the Division of Materials Science and Technology of the CSIR in Pretoria, South Africa.

Table 2
Relevant bond distances (Å) and angles (°) for **1**

Bond distances			
Re–Cl	2.393(9)	Re–P(1)	2.431(9)
Re–N(1)	1.98(3)	Re–N(1′)	1.97(3)
Re–N(2)	1.96(2)	Re–N(2′)	1.98(3)
Bond angles			
N(1)–Re–N(2)	77(1)	N(1′)–Re–N(2′)	79(1)
Re–N(1)–C(1)	120(2)	Re–N(1′)–C(1′)	115(2)
Re–N(2)–C(6)	121(2)	Re–N(2′)–C(6′)	117(2)
Cl–Re–N(1)	139.1(8)	Cl–Re–N(1′)	129.4(8)
P(1)–Re–N(2)	130.2(7)	P(1)–Re–N(2′)	135.3(8)
N(1)–Re–N(2′)	130(1)	N(1′)–Re–N(2)	144(1)

3. Results and discussion

3.1. Synthesis

The reaction of *trans*-$ReOCl_3(PPh_3)_2$ with 3-nitro-1,2-diaminobenzene (H_2L^1) in a 1:2 molar ratio in boiling ethanol gave the product $[ReCl(PPh_3)(L^1)_2]$ (**1**) in good yield:

$$ReOCl_3(PPh_3)_2 + 2H_2L^1 \underset{\Delta}{\overset{EtOH}{\rightarrow}} [ReCl(PPh_3)(L^1)_2] + 2HCl + H_2O + PPh_3$$

However, when *trans*-$ReOCl_3(PPh_3)_2$ was reacted with 4-nitro-1,2-diaminobenzene (H_2L^2) under the same conditions as for complex **1**, the imido complex $[Re(L^2)Cl_3(PPh_3)_2]$ (**2**) was isolated:

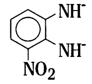
$$ReOCl_3(PPh_3)_2 + H_2L^2 \underset{\Delta}{\overset{EtOH}{\rightarrow}} [Re(L^2)Cl_3(PPh_3)_2] + H_2O$$

The formulation and structure of complexes **1** and **2** were verified by ^1H NMR spectrometry, IR spectroscopy, elemental analyses, and with regard to complex **1**, X-ray crystallography.

Both complexes are air stable and diamagnetic, and they are non-electrolytes in acetonitrile and DMF. Complex **1** is very soluble in a variety of solvents such as dichloromethane, acetone, acetonitrile, chloroform and ethyl acetate. The solubility of **2** in most polar solvents is low, but it can be crystallized from ethyl acetate and acetonitrile. Both complexes are stable in solution for days, and for months in the solid state.

3.2. Description of the structure of $[ReCl(PPh_3)(L^1)_2]$ (1)

The crystal structure shows that **1**·EtOH (Fig. 1) is monomeric and neutral, and exhibits the skew-trapezoidal bipyramidal geometry. The complex contains two dinegative L^1 ligands symmetrically coordinated to the Re(V) centre. The coordinating mode of L^1 (shown below) is evidenced by the four Re–NH bond distances



(all equal within the range of the e.s.d. values; mean value of 1.98(2) Å), which are consistent with the values found for this particular bond in eight Re(V) octahedral complexes (14 entries with a mean value of 2.00(1) Å) [11]. The Re–P bond (2.431(10) Å) is shorter than in other Re(V) complexes [12], probably because of the absence of an atom *trans* to it. The Re–Cl bond length (2.393(9) Å) is within the range observed for a large variety of Re(V) oxo, nitrido and imido complexes [6,11]. The Re, Cl and P(1) atoms are above the N(1), N(2), N(1′), N(2′) mean plane by 0.72, 2.51 and 2.57 Å, respectively. The two L^1 ligands make a dihedral angle of 60.3°.

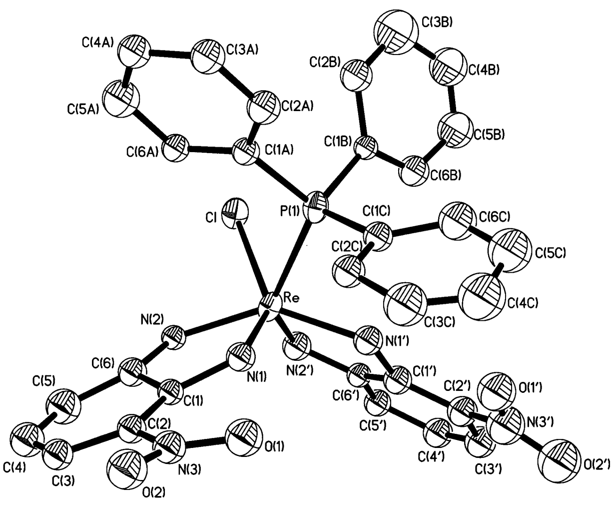


Fig. 1. The molecular structure of [ReCl(PPh$_3$)(L^1)$_2$] (**1**) showing the atom-numbering scheme and 40% displacement ellipsoids.

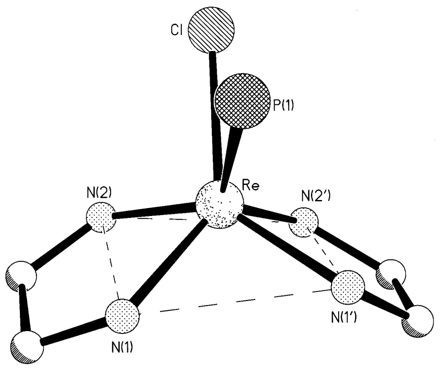


Fig. 2. Skew-trapezoidal bipyramidal arrangement of the donor atoms around Re(V) in complex **1**.

The two stereochemistries usually envisaged for six-coordinate complexes of the type [M(bidentate)$_2$-(unidentate)$_2$] are the *cis*- and *trans*-octahedral structures. However, both these structures become significantly distorted for bidentate ligands of small normalized bite [$b = 2\sin(i - \mathrm{M} - j/2)$]. The *trans*-octahedral structure distorts to form the skew-trapezoidal bipyramidal structure [13]. Surprisingly, this geometry occurs in **1** with a rather great value of the normalized bite [$b = 2\sin(\mathrm{N(1)-Re-N(2)}/2) = 1.26$].

Bidentate ligands that form the five- or six-membered chelate rings and have relatively large normalized bites ($b \sim 1.3$–1.5) normally form undistorted *trans* structures. As the normalized bite is decreased, however, energy calculations [14] show that the rectangle formed by the two coplanar bidentate ligands becomes distorted and forms a planar trapezoid. The unidentate ligands are simultaneously skewed towards, or even apart, the long edge of the trapezoid (Fig. 2).

In six-coordinate complexes of known crystal structure having two identical bidentate ligands, there is a marked preference for compounds with small normalized bite ligands (< 1.30) to form the *cis*-octahedral structure. However, the *trans* structure remains possible at low b when the effective bond length ratio, R (unidentate/bidentate) > 1.0 [14].

Examples of six-coordinate complexes of the type [M(bidentate)$_2$(unidentate)$_2$] with the skew-trapezoidal bipyramidal structure are scarce in the literature, and the few that were found are the tin(IV) complexes given in Table 3, together with their values of the normalized bite b and effective bond length ratio R.

The bidentate dianionic diamido coordination mode is quite common in the coordination chemistry of 1,2-diaminobenzene (H$_2$L^3) with transition metals, as the examples [UO$_2$(L^3)$_2$](NO$_3$)$_2$ [19], [Tc(L^3)$_3$](TcO$_4$) [20] and [Re(L^3)$_3$] [21] verify.

3.3. Spectroscopic properties

3.3.1. Complex 1

In the infrared spectrum of complex **1** there is no band observed in the region 900–1000 cm^{-1} which can be ascribed to the Re=O stretching frequency, indicating the absence of the oxo group. Two N–H absorptions occur at 3332 and 3284 cm^{-1}, which is consistent with the two inequivalent N–H protons of L^1. The ν_s(NO$_2$) is assigned to a sharp band at 1339 cm^{-1} (1430 cm^{-1} in the free ligand H$_2$L^1). The Re–N bands occur at 433 and 463 cm^{-1}, and the Re–Cl stretching frequency appears as a band of medium intensity at 301 cm^{-1}.

The proton NMR spectrum of **1** clearly indicates the presence of two chemically equivalent molecules of L^1 and one triphenylphosphine group. The triplet at 6.96 ppm integrates for two protons, and it is assigned to the 2 equiv. H^5 protons on the two phenylene rings. The doublets at 7.64 and 7.69 ppm integrate for two protons each, and are assigned to protons H^6 and H^4, respectively. The protons of the PPh$_3$ group appear as two multiplets at 7.12 and in the region 7.37–7.49 ppm, which integrate for six and nine protons, respectively.

Table 3
Complexes of the type [M(bidentate)$_2$(unidentate)$_2$] with the skew–trapezoidal bipyramidal structure (b = normalized bite; R = effective bond length ratio)

Complex	b	R	Ref.
ReCl(PPh$_3$)(L^1)$_2$	1.26	1.22	this work
Sn(NO$_3$)$_2$Me$_2$	0.92	1.20	[15]
Sn(S$_2$CNMe$_2$)$_2$Me$_2$	1.06	1.20	[16]
Sn{S$_2$P(OEt)$_2$}$_2$Ph$_2$	1.14	1.29	[17]
Sn(ONHCMeO)$_2$Me$_2$	1.17	1.12	[18]

The signals of the four N*H* protons appear as two singlets at 13.21 and 13.59 ppm, that each integrates for two protons. These latter two signals disappear on the addition of D_2O to the sample solution.

The infrared and NMR data unambiguously establish the fact that the two H_2L ligands in **1** are doubly deprotonated, with the result that the rhenium in **1** is in the formal oxidation state +V.

3.4. Complex 2

The infrared spectrum of complex **2** displays the Re=NR stretching frequency at 1092 cm^{-1}. There is no band in the region 900–1000 cm^{-1} which can be attributed to ν(Re=O), indicating the replacement of the oxo oxygen by the imido group. The two medium intensity bands at 3390 and 3195 cm^{-1} [$\nu(NH_2)$], and the appearance of $\delta(NH_2)$ at 1631 cm^{-1} indicate the presence of an uncoordinated amino group in **2**. In the far infrared region the ν(Re–Cl) appears as medium bands at 312 and 295 cm^{-1}, with the lower band indicative of the chloride coordinated *trans* to the rhenium imido bond.

In the ^1H NMR spectrum the signals of the H^6, H^3 and H^5 protons of L^2 are seen clearly at 6.38 (doublet), 6.86 (singlet) and 8.10 ppm (doublet), respectively. The two multiplets at 7.44 and 7.91 ppm integrate for 18 and 14 protons, respectively, with the latter overlapping the proton signal of the uncoordinated NH_2 group. This particular signal was previously found [6] in the range 6.50–7.32 ppm.

These results indicate that L^2 coordinates in a dianionic monodentate imido form to rhenium(V). Although it was impossible to establish which nitrogen (1 or 2) is coordinated to the metal, we speculate that due to the mesomeric effect of the 4-nitro group, the basicity of the 1-amino group will be reduced due to the increased delocalization of the 1-nitrogen's lone pair over the aromatic ring system, with the effect that the 2-nitrogen will be deprotonated and coordinated in the imido form to the metal.

Although **1** is the first example of a rhenium(V) complex with a bidentate diamido ligand, there are examples of oxo-free Re(V) complexes containing bidentate nitrogen-donor ligands, that were synthesized from *trans*-$ReOCl_3(PPh_3)_2$, in the literature. The reaction of $ReOCl_3(PPh_3)_2$ with (*o*-aminophenyl)diphenylphosphine (H_2L) in toluene yielded the neutral rhenium(V) complex $[ReCl_2(L)(HL)]$. Both ligands are coordinated bidentately, with L^{2-} bonded as a P,N-donor ligand with an imido nitrogen (Re=N length = 1.757(4) Å), and the second HL^- ligand containing an amido nitrogen (Re–N bond length = 1.988(4) Å) [22,23]. The reaction of $ReOCl_3(PPh_3)_2$ with thiosemicarbazides $RNHCSNHNH_2$ (R = Me, Ph) in ethanol in the presence of aqueous HCl and triphenylphosphine gave the rhenium(V) S,N-chelated thiosemicarbazate(3–) complexes $[ReCl_2(NNCSNHR)(PPh_3)_2]$ [24].

4. Concluding remarks

The isolation of complex **1** presents a very interesting example of an oxo-free complex of rhenium(V), which was surprisingly easily prepared from the oxo complex *trans*-$ReOCl_3(PPh_3)_2$. The substitution of an oxo group from rhenium(V) is not often observed, and rhenium(V) complexes lacking a multiply bonded donor atom as ligand are unusual. Complex **2** presents another example of the unusual monodentate imido formation of 1,2-diaminobenzenes in complexes of rhenium(V).

5. Supplementary material

Crystallographic data (comprising detailed information on structure data collection and structure refinement, final fractional atomic coordinates, thermal parameters and a full listing of bond lengths/angles) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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