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Synthesis, structure and chemistry of vanadium(IV) and vanadium(V) compounds with substituted hydrazido(1−) and hydrazido(2−) ligands

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The reaction of [V(NS_3)O] [$NS_3 = N(CH_2CH_2S)_3$] with methylhydrazine gives the hydrazido(1−) vanadium(IV) complex [V(NS_3)(NMeNH_2)] **1**, but reaction with various other compounds containing N–N groups results in formation of compounds containing substituted hydrazido(2−) ligands. Structures of **1**, [V(NS_3)(NNC_5H_{10})] **2** and [V(NS_3)($NNCPh_2$)] **3** are described.

Introduction

Hydrazido(2−) ligands $(NNH_2)^{2-}$ are well known in molybdenum-phosphine chemistry as products of the partial reduction of dinitrogen ligands,[1] and have also been found in the general chemistry of molybdenum, tungsten and other early transition metals with various co-ligands.[2] There are, however, relatively few structurally characterised hydrazide complexes of vanadium.[3] Hydrazine ligands in vanadium complexes are also rare.[4] Recently we[5] have been investigating the reactions of vanadium complexes derived from the tris(2-thiolatoethyl)-amine ligand $N(CH_2CH_2S)_3{}^{3-}$ (NS_3) with the aim of investigating the potential of this site to activate the reduction of N_2, and have reported preparations of several complexes containing V–N–N systems obtained by treating the oxide [V(NS_3)O] with compounds containing N–N bonds. Thus reaction of [V(NS_3)O] with N_2H_4 gives the adduct [V(NS_3)(N_2H_4)], probably *via* the intermediate [V(NS_3)(NNH_2)]. In contrast, reaction of [V(NS_3)O] with mono- and di-substituted hydrazines NH_2NR_2 (R_2 = MePh, Me_2, HPh) gives no reduction and yields the diamagnetic vanadium(V) complexes [V(NS_3)(NNR_2)]. Here we report further reactions of [V(NS_3)O] with other compounds containing the NH_2 grouping, which have yielded, *inter alia*, a hydrazido(1−) complex of vanadium(IV).

Results and discussion

Treatment of [V(NS_3)O] with an excess of methylhydrazine either neat or in ethanol solution followed by addition of diethyl ether led to the isolation of X-ray quality crystals of the vanadium(IV) complex [V(NS_3)(NMeNH_2)] **1**. The same compound was obtained by the reaction of [V(NS_3)($NNMe_2$)] with methylhydrazine. Although one (N–H) hydrogen atom of the NMeNH_2 ligand was not found in the structure, Fig. 1, the magnetic moment of **1** establishes it as vanadium(IV) in the solid state, and the geometry of the NMeNH_2 ligand is consistent with the above formulation of complex **1**, as detailed below. Principal dimensions in the three complexes analysed are listed in Table 1.

The coordination of the vanadium atom in **1** is trigonal bipyramidal, with V–N distances of 2.145(6) Å to the hydrazide ligand, and 2.165(6) Å to the nitrogen atom in the NS_3 ligand; the N–V–N angle is 178.6(2)°. These dimensions are comparable to those in the vanadium(III) complex [V(NS_3)(N_2H_4)] but quite different from those in the vanadium(V) complexes [V(NS_3)(NNR_2)].[5] In the latter compounds the distance from the vanadium to the coordinating N in the hydrazide ligands is always < 1.7 Å indicating the presence of a V–N double bond, while the distance from the vanadium to the coordinating N in the NS_3 ligand is > 2.2 Å, reflecting the strong *trans*-effect of this V=N bond. Also the N–N distance in **1** is 1.427(9) Å, slightly shorter than the 1.48(2) Å and 1.46(2) Å found in [V(NS_3)(N_2H_4)] (major and minor components) but much longer than those found in the [V(NS_3)(NNR_2)] complexes [1.305(5) Å for $R_2 = Me_2$ and 1.310(3) Å for R_2 = MePh] and in other vanadium(V)-hydrazido(2−) complexes *e.g.* [V($OC_6H_3Pr^i{}_2$-2,6)$_3$($NNMe_2$)] [1.311(4) Å].[4] The V–N(hydrazide) bond in **1** is thus definitely a single bond, and the N–N

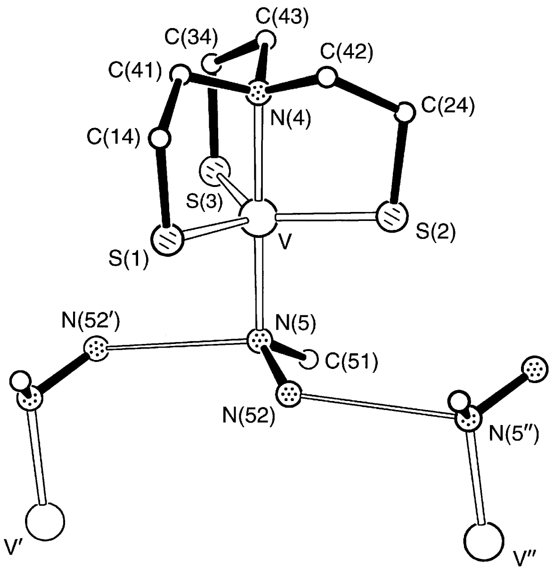

Fig. 1 View of a molecule of [V(NS_3)(NMeNH_2)], **1** and its hydrogen bond connections to adjacent molecules. Hydrogen atoms in the NS_3 ligand have been omitted (in all the figures) for clarity. One hydrogen atom bound to N(52) was located; a second hydrogen atom in the hydrazide ligand was not located but is expected to lie close to the N(5) ··· N(52′) hydrogen bond, close to either nitrogen atom.

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Table 1 Comparison of selected molecular dimensions (Ångstroms and degrees) in complexes **1**, **2**·0.5CD_2Cl_2 and **3**

Complex	[$V(NS_3)(NMeNH_2)$], **1**	[$V(NS_3)(NNC_5H_{10})$]·0.5CD_2Cl_2, **2**·0.5CD_2Cl_2	[$V(NS_3)(NNCPh_2)$], **3**
Mean V–S	2.281(3)	2.261(4)	2.264(4)
V–N(NS_3)	2.165(6)	2.216(2)	2.223(2)
Mean V–N–S in NS_3 ligand	86.2(3)	84.47(5)	84.16(9)
N–V–N	178.6(2)	179.23(10)	176.08(7)
V–N(hydrazide)	2.145(6)	1.677(2)	1.691(2)
N–N	1.427(9)	1.324(3)	1.311(2)
V–N–N	112.5(5)	177.0(2)	167.00(14)

Other dimensions in the hydrazide ligands:

Complex **1**		Complex **2**·0.5CD_2Cl_2		Complex **3**	
N(5)–C(51)	1.487(10)	N(51)–C(52)	1.445(4)	N(6)–C(6)	1.306(2)
V–N(5)–C(51)	117.1(5)	N(51)–C(56)	1.441(4)	C(6)–C(611)	1.473(2)
N(52)–N(5)–C(51)	104.8(7)	N(5)–N(51)–C(52)	116.2(3)	C(6)–C(621)	1.482(3)
N(5) ··· N(52′)	3.066(10)	N(5)–N(51)–C(56)	116.8(2)	N(5)–N(6)–C(6)	121.2(2)
		C(52)–N(51)–C(56)	114.3(3)	N(6)–C(6)–C(611)	116.8(2)
				N(6)–C(6)–C(621)	123.8(2)
				C(611)–C(6)–C(621)	119.4(2)

N.B. The prime indicates the symmetry operation: $x - 1/2, 1/2 - y, 1 - z$.

bond in **1** is a slightly shortened single bond rather than a double bond.

In the crystal, there are hydrogen bonds linking molecules in chains parallel to the *a* axis, Fig. 1; the hydrogen atom involved has not been located but could be on either nitrogen atom. The conformation about both nitrogen atoms is tetrahedral and the bonds are staggered.

When **1** is treated with excess hydrazine hydrate, it is converted quantitatively to the vanadium(III) complex [$V(NS_3)(N_2H_4)$]. Other reactions of **1** are comparable to those of this vanadium(III) complex. Thus **1** reacts with trimethylamine oxide giving [$V(NS_3)O$], and with cyclohexyl isocyanide giving [$V(NS_3)(CNCy)$], while prolonged heating at reflux temperature in MeCN yields a mixture of [$V(NS_3)(MeCN)$] and the polymeric insoluble material $\{V(NS_3)\}_n$. Treatment of **1** with HBF_4·Et_2O in MeCN also yields $\{V(NS_3)\}_n$ accompanied by some [$V(MeCN)_6$]$(BF_4)_3$. These reactions obviously involve the release of the methylhydrazido ligand which must act as a reducing agent for vanadium(IV) to vanadium(III) but we have not monitored its fate.

We also treated **1** with NO gas under conditions similar to those used to make [$Mo(NS_3)(NO)$][6] and with *N*-hydroxybenzenesulfonamide (Piloty's acid)[7] obtaining an inseparable mixture of a compound with a strong IR band at 1693 cm^{-1} (possibly the desired complex [$V(NS_3)(NO)$]) and [$V(NS_3)O$] with ν(VO) at 976 cm^{-1}.[8]

The reduction of [$V(NS_3)O$] to a vanadium(IV) product by methylhydrazine contrasts with the reduction with hydrazine which gives the vanadium(III) compound [$V(NS_3)(N_2H_4)$] and also with the reaction with phenylhydrazine which does not proceed below 140 °C but at this temperature gives a vanadium(V) product [$V(NS_3)(NNHPh)$]. It is thus possible to make vanadium-NS_3 complexes with a range of oxidation states from V^{III} to V^V. In an effort to extend this range we treated [$V(NS_3)O$] with a selection of other compounds containing the NNH_2 group such as hydrazones R_2CNNH_2 or hydrazides $RCONHNH_2$, either without use of solvent or in 2-methoxyethyl ether (diglyme).

The reaction of [$V(NS_3)O$] with 1-aminopiperidine at about 140 °C gave the hydrazido(2−) complex [$V(NS_3)(NNC_5H_{10})$] **2** which is analogous to vanadium(V) compounds prepared using phenylhydrazine, 1,1-dimethylhydrazine and 1-methyl-1-phenylhydrazine.[5] The V–N(hydrazide) distance in **2**, Fig. 2, is 1.677(2) Å (V–N double bond), the N–N distance is 1.324(3) Å, and the V–N–N (hydrazide) angle is almost linear at 177.0(2)°.

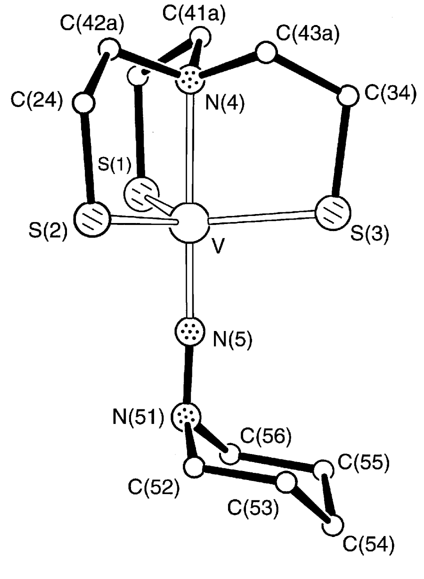

Fig. 2 View of a molecule of [$V(NS_3)(NNC_5H_{10})$], **2**, in crystals of **2**·0.5CD_2Cl_2, showing the major component of the disordered NS_3 ligand.

[$V(NS_3)O$] reacted with benzophenone hydrazone $Ph_2C{=}NNH_2$ at 160 °C with some decomposition to give $\{V(NS_3)\}_n$, but also a red solution from which [$V(NS_3)(NNCPh_2)$] **3** precipitated on cooling. There is considerable delocalisation over the V–N–N–C system in **3**, Fig. 3, as shown by the relevant bond lengths and angles. The V–N(hydrazide) distance is 1.691(2) Å (V–N double bond), the N–N distance is 1.311(2) Å and the N–C distance is 1.306 Å. The V–N–N(hydrazide) angle is 167.0(1)°, N–N–C is 121.2(2)°, and the angles about the C atom are 116.8(2), 123.8(2) and 119.4(2)° giving planar trigonal bonding. These dimensions are very similar to those found in [*p*-Bu^t-calix[4]-$(OMe)(O)_3V(NNCPh_2)$].[9]

Complexes **2** and **3** are both diamagnetic vanadium(V) complexes. Their ^1H and ^{51}V NMR spectra are characteristic of vanadium(V) species, the vanadium chemical shifts being comparable to those found for complexes such as [$V(NS_3)(NNHPh)$] (δ 401, fwhm = 820 Hz).[5] The V–N(NS_3) distances of 2.216(2) Å in **2** and 2.223(2) Å in **3** are also characteristic of this distance in V^V-NS_3 complexes.[5] Unlike **1**, complexes **2** and **3** did not react with trimethylamine oxide with displacement of the hydrazido ligand.

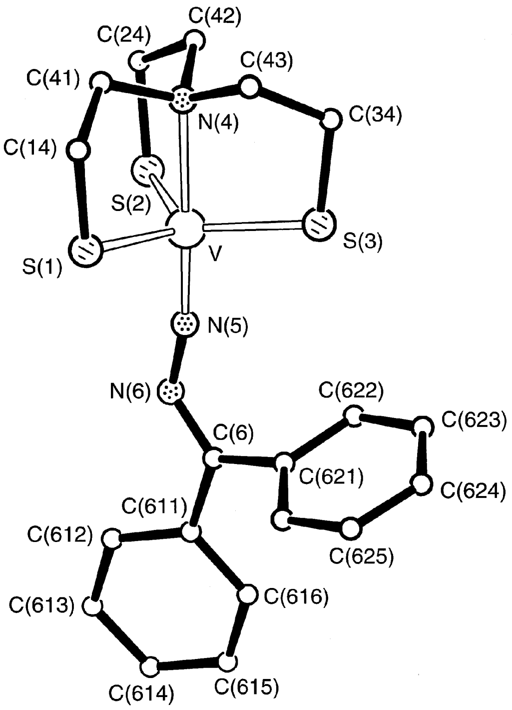

Fig. 3 View of a molecule of [V(NS$_3$)(NNCPh$_2$)], **3**.

In contrast to the reaction with benzophenone hydrazone, treatment of [V(NS$_3$)O] with salicylaldehyde hydrazone at 160 °C resulted in displacement of the NS$_3$ ligand to give tris(salicylaldehyde hydrazonato)vanadium(III) which has been prepared from [VCl$_3$(thf)$_3$] by treatment with salicylaldehyde and hydrazine.[10]

Benzoic hydrazide PhCONHNH$_2$ reacted with [V(NS$_3$)O] at 140 °C giving a yellow solution and a green precipitate of $\{V(NS_3)\}_n$ *i.e.* there was reduction and no V–N bond formation. The same product was observed when [V(NS$_3$)O] was treated with either hydroxyethylhydrazine or pentafluorophenylhydrazine, under comparable conditions.

[V(NS$_3$)O] did not react with two other compounds containing the NNH$_2$ group, 4-amino-1,2,4-triazole and *N*-aminophthalimide, at 160 °C. Attempts to heat solutions or suspensions of [V(NS$_3$)O] (with or without other reactants) at temperatures higher than 160 °C [by using benzonitrile (bp 170 °C) or ethylene glycol (bp 192 °C) at reflux temperatures] resulted in rapid decomposition to give insoluble materials including $\{V(NS_3)\}_n$. The vanadium(V) compound [V(NS$_3$)(NSiMe$_3$)],[5] which is more soluble in ethers or in MeCN than is [V(NS$_3$)O], was also treated with some of the above compounds containing NNH$_2$ groups in an attempt to form V–N–N bonds at lower temperatures, but in every case the product formed was [V(NS$_3$)(NH)][5] by abstraction of one of the active hydrogens from the NNH$_2$ group.

Thus it is possible to make some compounds containing V–N–N systems using [V(NS$_3$)O] and substituted hydrazines or hydrazones as starting materials, but reactions targeted to obtain V–N–N bonds must compete with reduction of the vanadium(V) oxide to vanadium(III) which results in formation of the polymeric $\{V(NS_3)\}_n$ or in complete displacement of the NS$_3$ ligand.

Experimental

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled under dinitrogen from the appropriate drying agents prior to use. Preparations of the ligand NS$_3$H$_3$ and of [V(NS$_3$)O], as well as spectroscopic and magnetic measurements, were made as described previously.[5]

Syntheses

[V(NS$_3$)(NMeNH$_2$)], 1. Methylhydrazine (4 ml, excess) was added to [V(NS$_3$)O] (1.31 g, 5 mmol). A vigorous reaction took place resulting in a red solution; this was filtered and ether (96 ml) added to the filtrate which was kept at −20 °C overnight. Red crystals suitable for X-ray studies (1.32 g, 90%) were filtered off. Found: C, 28.9; H, 5.8; N, 15.8. C$_7$H$_{17}$N$_3$S$_3$V requires C, 29.0; H, 5.9; N, 14.5%. $\mu_{\text{eff}} = 1.81\ \mu_B$ ($S = 1/2$). IR 3337, 3154 cm^{-1} [ν(NH)].

[V(NS$_3$)(NNC$_5$H$_{10}$)], 2. *N*-Aminopiperidine (5 ml, excess) was added to [V(NS)$_3$)O] (0.52 g, 2 mmol). The mixture was heated to 140 °C when a vigorous reaction took place resulting in a red solution; this was cooled overnight giving orange crystals (0.53 g, 78%). Found: C, 38.7; H, 6.4; N, 12.3. C$_{11}$H$_{22}$N$_3$S$_3$V requires C, 38.5; H, 6.5; N, 12.2%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.58 (m, 2H, CH_2), 1.84 (m, 4H, CH_2), 3.39 (m, 6H, NCH_2CH_2S), 3.45 (m, 6H, NCH_2CH_2S), 3.85 (m, 4H, CH_2). ^{51}V NMR (CD$_2$Cl$_2$): δ 401, fwhm = 820 Hz. X-Ray quality crystals were obtained by recrystallisation from CH$_2$Cl$_2$.

[V(NS$_3$)(NNCPh$_2$)], 3. Benzophenone hydrazone (0.98 g, 5 mmol) was added to [V(NS)$_3$)O] (0.13 g, 0.5 mmol) in diglyme (10 ml). The mixture was taken to reflux temperature (162 °C) for 30 minutes, during which time the colour changed from purple to orange. The solution was allowed to cool overnight and was filtered from a small black precipitate, then the volume of filtrate was reduced *in vacuo* at 60 °C to 4 ml when red crystals (0.10 g, 45%) deposited. Found: C, 52.5; H, 5.0; N, 9.6. C$_{19}$H$_{22}$N$_3$S$_3$V requires C, 51.9; H, 5.0; N, 9.6%. ^{1}H NMR (CD$_2$Cl$_2$): δ 3.46 (m, 6H, NCH_2CH_2S), 3.61 (m, 6H, NCH_2CH_2S), 7.50 (m, 6H, Ph), 7.80 (m, 4H, Ph). ^{51}V NMR (CD$_2$Cl$_2$): δ 437, fwhm = 1060 Hz. X-Ray quality crystals were obtained by recrystallisation from acetonitrile.

Crystal structure analyses

The crystal structure analysis of [V(NS$_3$)(NNC$_5$H$_{10}$)]·0.5CD$_2$Cl$_2$, **2**·0.5CD$_2$Cl$_2$, is described here. The two other analyses followed very similar procedures and crystal data for the three structures are listed in Table 2.

Crystals of **2** are deep red, striated plates. One, *ca.* 0.10 × 0.43 × 0.55 mm, was mounted, in air, on a glass fibre. After preliminary photographic examination, this was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections, θ = 10–11°, each centred in four orientations) and for measurement of diffraction intensities (3835 unique reflections to $\theta_{\max} = 27°$; 2778 were 'observed' with $I > 2\sigma_I$).

During processing, corrections were applied for Lorentz-polarisation effects, absorption (by semi-empirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods). No deterioration correction was necessary. The structure was determined by the direct methods routines in the SHELXS program[11] and refined by full-matrix least-squares methods, on F^2 in SHELXL.[12] The vanadium complex was well-resolved and showed disorder in the NS$_3$ ligand with the major/minor component ratio of 0.695(5) : 0.305. Hydrogen atoms were included, on both components and on the piperidine ring, in idealised positions. The non-hydrogen atoms (except those of the minor component) were refined with anisotropic thermal parameters and the H-atom U_{iso} values were set to ride on the U_{eq} or U_{iso} values of the parent carbon atoms. There is also a solvent (CD$_2$Cl$_2$) molecule, disordered over several orientations about a centre of symmetry; these part-atoms (with a range of site occupancies) were refined isotropically, and no hydrogen/deuterium atoms were included. At the conclusion of the refinement, $wR2 = 0.116$ and $R1 = 0.056$[12] for all 3835 reflections weighted $w = [\sigma^2(F_o^2) +$

Table 2 Crystal and structure refinement data for the three vanadium complexes

Complex	$[V(NS_3)(NMeNH_2)]$, **1**	$[V(NS_3)(NNC_5H_{10})]\cdot 0.5CD_2Cl_2$, **2**·$0.5CD_2Cl_2$	$[V(NS_3)(NNCPh_2)]$, **3**
Elemental formula	$C_7H_{17}N_3S_3V$	$C_{11}H_{22}N_3S_3V$, $1/2(CD_2Cl_2)$	$C_{19}H_{22}N_3S_3V$
Formula weight	290.4	385.9	439.5
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_1/a$ (equiv. to no. 14)	$P2_1/n$ (equiv. to no. 14)
a/Å	7.7299(11)	11.4660(10)	7.5275(7)
b/Å	9.736(2)	11.9468(12)	15.350(2)
c/Å	16.638(3)	12.8618(13)	17.491(2)
β/°	90	91.595(8)	98.709(8)
V/Å^3	1252.2(4)	1761.2(3)	1997.8(3)
Z	4	4	4
F(000)	604	804	912
Absorption coefficient/mm^{-1}	1.260	1.063	0.818
Crystal colour, shape	Brown–orange, flat needles	Red, striated plates	Blood red, hollow square tubes
Crystal size/mm	0.76 × 0.11 × 0.10	0.55 × 0.43 × 0.10	0.48 × 0.24 × 0.24
Total no. of reflections measured (not including absences)	1771	4302	6583
R_{int} for equivalents	0.035	0.025	0.022
Total no. of unique reflections	1288	3835	5814
No. of 'observed' reflections ($I > 2\sigma_I$)	1136	2778	3978
Data/restraints/parameters	1288/2/132	3835/0/204	5814/0/323
Final R indices ('observed' data)	$R1 = 0.055$, $wR2 = 0.130$	$R1 = 0.039$, $wR2 = 0.102$	$R1 = 0.037$, $wR2 = 0.079$
Final R indices (all data)	$R1 = 0.061$, $wR2 = 0.136$	$R1 = 0.056$, $wR2 = 0.116$	$R1 = 0.061$, $wR2 = 0.092$
Reflections weighted:[a] $w =$	$[\sigma^2(F_o^2) + (0.0928P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0538P)^2 + 0.56P]^{-1}$	$[\sigma^2(F_o^2) + (0.0212P)^2 + 0.49P]^{-1}$

All intensity meaurements at 293(1) K, with Mo-Kα radiation $\lambda = 0.71069$ Å.[a] Where $P = (F_o^2 + 2F_c^2)/3$.

$(0.0538P)^2 + 0.56P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, $R1 = 0.039$.

In the final difference map, the highest peaks (to *ca.* 0.3 e Å^{-3}) were close to the vanadium atom.

Scattering factors for neutral atoms were taken from ref. 13. Computer programs used in this analysis have been noted above or in Table 4 of ref. 14, and were run on a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

CCDC reference numbers 180740–180742.

See http://www.rsc.org/suppdata/dt/b2/b202098j/ for crystallographic data in CIF or other electronic format.

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