Substituted Variants of the Cluster Type $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$

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Various aromatic nitriles were used for the preparation of the nitrile-capped clusters $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$ (**2**) by reaction with $Fe_3(CO)_{12}$ under hydrogen. Electron-rich nitriles decrease, electron-poor nitriles increase the thermal stability of clusters **2**. With CN-substituted pyridines only traces of clusters **2** could be obtained. CO replacement in $Fe_3(CO)_9(PhCN)$ (**2a**) by isonitriles also causes a lowering of the stability. Conversely, more stable products were obtained by substitution reaction with trimethyl phosphite. One PPh_3 and two dppm derivatives were also obtained. The structure of $Fe_3(CO)_8\text{-}P(OMe)_3(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}N)$ (**5a**) was determined.

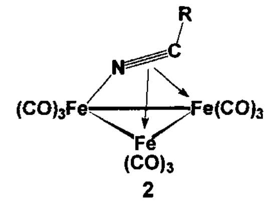
The nitrile unit is one of the important functional units in synthetic organic chemistry. In the context of organometallic cluster chemically and the cluster/surface analogy it should therefore be interesting to find out whether attachment of a nitrile to several metal atoms can induce new types of reactivity derived from its CN function. In order to test this, clusters with capping nitrile ligands of various kinds should be available in sufficient quantity.

Previous investigations in this field by Kaesz[1−4] and ourselves[5−7] have led to the benzonitrile variant and two aliphatic nitrile variants of the basic cluster type **2** and a detailed study of the hydrogenation/dehydrogenation processes involving the RCN units in the ligand sphere. To our knowledge no other complex of type **2**, no CO-substituted derivative thereof, and no organic reaction in the ligand sphere of clusters **2** have been published so far, but other groups have reported on the reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with nitriles[8,9].

We therefore set out to create a broader basis for this kind of investigations by synthesizing iron clusters capped with various nitriles and CO-substituted derivatives thereof. The main goal was to find out the factors which determine the stability of the clusters derived from **2** or their nitrile constituents **1**, respectively.

$N{\equiv}C{-}R$

1



2

New clusters $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$ (2)

The only procedure that has been found so far to incorporate nitriles directly into the triiron cluster involves reaction of $Fe_3(CO)_{12}$ with the nitriles while bubbling hydrogen through the solution[5]. As the nitrile is not hydrogenated under these conditions it must be assumed that unstable cluster hydrides like $H_2Fe_3(CO)_9$ are intermediates. We have verified now that this procedure works for aromatic nitriles only and that other modes of activating the cluster for the capping reaction are less efficient. Thus, attempts to use UV radiation, amine oxides or radical starters for activation failed, and the use of solvents other than hydrocarbons only resulted in a decrease of the yields of clusters **2**. The optimum yields were obtained in boiling cyclohexane. In each case the course of the reaction had to be monitored by IR to find the optimal situation between consumption of the starting materials and decomposition of the products.

$R{-}C{\equiv}N$ **1a−k** $\qquad Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$ **2a−k**

	R		R		R
a	Ph	**e**	2-CN-Ph	**i**	C_6F_5
b	4-Me-Ph	**f**	3-CN-Ph	**j**	2-CN-Py
c	4-Me_2N-Ph	**g**	4-CN-Ph	**k**	4-CN-Py
d	4-MeO-Ph	**h**	3-CF_3-Ph		

After optimizing the synthesis[5] of the known cluster **2a** and finding out that aliphatic nitriles cannot be incorporated in this way the synthetic procedure was applied to electron-rich and electron-poor aromatic nitriles as well as to two pyridinecarbonitriles. Altogether the nitriles **1b**−**k** were converted to the clusters **2b**−**k**. Of these **2b**, **d**, **e**, **f**, and **i** were obtained analytically pure, and the compositions of **2c** and **g** could be ascertained by mass spectral analysis. Compounds **2h**, **j**, and **k** could only be identified by their spectra which in the case of **2j** and **k** is due to their extremely low yields.

Except for **2b**, **d**, **h**, and **i** the yields of the clusters were disappointing. This reflects the fact that all clusters **2** slowly decompose under the conditions of their formation. Actually, all of the clusters **2a**−**g** decompose when kept at room temperature even under inert gas. The thermal stabilities of all clusters **2** seem to depend in a systematic manner on the nature of the nitrile ligands: those with electron-rich nitriles

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(**2b**–**d**) being less stable and those with electron-poor nitriles (**2e**–**i**) being more stable than the parent cluster **2a**. The clusters with the strongest electron-withdrawing nitriles **2h** and **i** are the only ones that can be stored at room temperature for longer periods. The trends in stability are also reflected in the melting points, but there is no relation between the yields of the compounds and their stabilities. A typical example of this are the clusters **2j** and **k** containing the cyanopyridine units which seem to be relatively stable but which could be obtained only in trace amounts.

In almost all cases the cluster **2** seemed to be the only product that was isolable under the applied conditions. This is noteworthy in the case of the dicyanobenzenes **1e**–**g** which offer two potentially face-capping nitrile units. Obviously, the electronic and steric demands of the triiron unit are such that they disable the bonding capacity of the second nitrile function. Similarly, the spectra of the cyanopyridine-capped clusters **2j** and **k** indicate that only the nitrile unit is attached to the triiron cluster. However, in this case it is likely that the pyridine function is responsible for the low yields of the compounds by playing a role in possible decomposition reactions.

CO Substitution in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$ (2)

Since cluster compounds in which CO is replaced by other donor ligands are often more stable than the parent clusters it was hoped that this would also be true for derivatives of **2**. With this in mind the simplest cluster **2a** and its most stable variant **2i** were treated with some isonitrile and phosphane ligands. The use of isonitriles, however, brought no improvement. The clusters **3a** and **4a**, formed from **2a** and the corresponding isonitrile at room temperature, were isolated only in low yields and were so unstable that they were decomposed before elemental analyses could be obtained.

$$Fe_3(CO)_8(RNC)(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}N)$$
$$\mathbf{3a}\text{: } R = 4\text{-}CH_3\text{-}Ph \quad \mathbf{4a}\text{: } R = t\text{-}Bu$$

Better results were obtained with phosphite and phosphane ligands. Both **2a** and **2i** were converted at room temperature to the more stable monophosphite derivatives **5a** and **5i**. While this could not be achieved for **2a** with triphenylphosphane, the reaction of **2i** with PPh_3 afforded **6i** in very good yield. All three new clusters are more stable than their parent compounds. Compound **5i**, is air-stable in solution for several hours. Derivatives of **2a** and **i** containing more than one PR_3 ligand could not be obtained. Instead, the application of more rigorous conditions or higher amounts of the appropriate PR_3 led to increased formation of the side products $Fe_3(CO)_{10}(PR_3)_2$ and $Fe_3(CO)_9(PR_3)_3$.

$$Fe_3(CO)_8P(OMe)_3(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}N) \qquad Fe_3(CO)_8PR_3(\mu_3\text{-}\eta^2\text{-}C_6F_5C{\equiv}N)$$
$$\mathbf{5a} \qquad \mathbf{5i}\text{: } R = OMe$$
$$\mathbf{6i}\text{: } R = Ph$$

It was, however, possible to introduce two PR_3 units as the chelating ligand bis(diphenylphosphino)methane (dppm). This again proved to be much easier for **2i** than for **2a** as evidenced by the high yield of **7i** in comparison with the modest yield of **7a**. The thermal and oxidative stabilities of **7a** and **i** are comparable to those of the other PR_3 derivatives.

$$Fe_3(CO)_7dppm(\mu_3\text{-}\eta^2\text{-}RC{\equiv}N)$$
$$\mathbf{7a}\text{: } R = Ph \quad \mathbf{7i}\text{: } R = C_6F_5$$

Product Identification

All clusters **2**–**7** are brown solids. Their simplest identification is by the IR spectra (see Table 1). Specifically, all eleven clusters **2** show highly similar IR patterns in the CO range securing the identity of **2j** and **2k** which could not be detected otherwise. The ν(CO) band positions of **2a**–**k** depend to a small extent (±10 cm^{-1}) on the electron-releasing/electron-withdrawing properties of the aryl substituent of $ArC{\equiv}N$ such that electron-rich ones shift them to lower wavenumbers and vice versa. The ν(CN) band of **3a** and **4a** is observed near 2150 cm^{-1}.

Table 1. IR data (ν_{CO}, cm^{-1}, in hexane) of the compounds **2**–**7**

2a	2085m	2038s	2029vs	2016s	2003w	1994m	1982w
2b	2084m	2037s	2028vs	2015s	2002w	1993m	1981w
2c	2080m	2033s	2025vs	2011s	1997w	1988m	1977w
2d	2083m	2035s	2026vs	2010s		1988m	1976w
2e	2089m	2042s	2034vs	2020s		1996m	1985w
2f	2088m	2041s	2033vs	2020s	2009w	1997m	1987w
2g	2088m	2041s	2033vs	2021s	2008w	1998m	1987w
2h	2088m	2041s	2033vs	2020s	2007w	1998m	1986w
2i	2091m	2048s	2036vs	2023s	2015w	2004m	1987m
2j	2075m		2025vs		2010m	2006s	1991m
2k	2088m	2041s	2032vs	2017s		1995m	1983w
3a	2144m	2056m	2020vs	1995m	1985m	1974m	1960w
4a	2162w	2057m	2016vs	1992m	1982m	1970m	1956w
5a	2059m	2016vs	2009s	1991m	1986m	1978m	1969w
5i[a]	2065s	2024vs	2016s	1992s	1979m	1965w	1956w
6i	2061s	2023vs	2010s	1987s	1978sh	1954w	1946w
7a[a]	2031vs	1987s	1969vs				
7i[a]	2039vs	1999vs	1979vs				

[a] In dichloromethane.

In the NMR spectra of all compounds (^1H, ^{13}C) the main features are the aromatic signals. Table 2 lists the spectroscopic data of the substituents (of the $RC{\equiv}N$ groups and of the donor ligands) which are of diagnostic value. They are all in their typical ranges. Except for **2i** and its derivatives **5i**, **6i** and **7i** all compounds show just one ^{13}C-NMR signal for the CO ligands thereby indicating CO fluxionality. To improve the identification of **2h** which could not be obtained analytically pure, a ^{19}F-NMR spectrum was recorded. It exhibits a single signal at $\delta = -63.4$ (internal standard $CFCl_3$).

Among the donor-substituted clusters **3**–**7** the positions of the isocyanide ligands in **3a** and **4a** could not be inferred from the spectra. The phosphane ligand of **5a**, **5i**, and **6i** is supposed to be located in the plane of the three iron atoms attached to the nitrogen-connected iron atom as secured for **5a** (see below). Assuming that this is also the case for one phosphorus atom in **7a** and **i** we can conclude that the chelating phosphane ligand is bound to two symmetry-inequivalent iron atoms. This is confirmed by the ^{31}P-NMR spectra of **7a** and **i** (see Table 3). In the ^{1}H- and ^{13}C-NMR spectra this is derived only for **7i** in the form of two different coupling constants J(P−X) while for **7a** broad signals possibly due to fluxionality obscure these features.

Table 2. ^{1}H- and ^{13}C-NMR data (in CD_2Cl_2, int. TMS, ppm, Hz)

	substituent	^{1}H-NMR δ (m, J)	^{13}C-NMR δ (m, J)
2b	Me	2.38(s)	30.1(s)
2c	Me_2N	3.12(s)	40.1(s)
2d	MeO	3.95(s)	55.7(s)
2e	CN	--	116.7(s)
2f	CN	--	116.1(s)
2g	CN	--	114.7(s)
2h	CF_3	--	123.4(q, 271)
3a	Me	2.34(s)	--
4a	t-Bu	1.18(s)	--
5a	OMe	3.76(d,12.1)	54.6(d, 5.1)
5i	OMe	3.79(d,12.0)	53.3(d, 5.0)
7a	$P-CH_2-P$	3.88(m), 3.08(m)	47.2(t, 19)
7i	$P-CH_2-P$	3.63(ddd, 13.4, 11.5, 2.8) 2.91(ddd, 13.4, 11.5, 2.8)	46.2(dd, 21, 16)

Table 3. ^{31}P-NMR data of clusters **5**−**7** (CD_2Cl_2, ext. H_3PO_4)

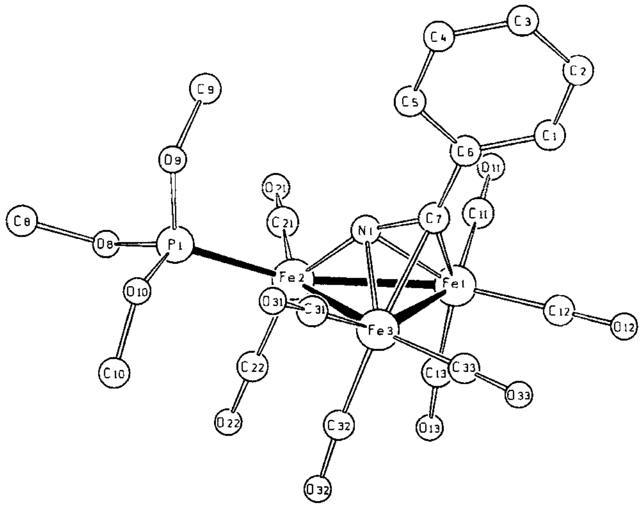
5a	172.4(m, 12)	
5i	168.2(m, 12)	
6i	64.7	
7a	63.6(d, 77),	49.8(d, 77)
7i	61.3(d, 64),	54.6(d, 64)

Although the mass spectra of the clusters **2**−**7** did not provide satisfactory data they were helpful in the identification of these compounds. EI-MS produced as highest masses for **2b** 481 (M^+ − 2 CO), for **2f** 548 (M^+), for **2g** 548 (M^+), for **2i** 557 (M^+ − 2 CO), and for **5a** 619 (M^+). The ion-spray technique yielded masses of 538 (M^+ − CO) for **2c** and 852 (M^+ + H) for **7a**. Application of the MALDI technique afforded a mass of 866 for **7i** resulting from the loss of 2 CO and 1 F from the parent ion.

A complete characterization of the structure and material for structural comparisons were obtained for the phosphite-substituted cluster **5a** by a crystal structure determination (Figure 1). For details see Experimental.

The general molecular features of **5a** are nearly identical with those of the parent clusters **2a**[5] and $Fe_3(CO)_9(\mu_3-\eta^2-C_3H_7C{\equiv}N)$[4]. This concerns the shape and bond lengths of the metal triangle as well as the mode of bonding and orientational details of the capping nitrile ligand. It is noteworthy that even the isocyanide-capped clusters $Fe_3(CO)_9(\mu_3-\eta^2-t\text{-}BuN{\equiv}C)$[10] and $Fe_3(CO)_8P(OMe)_3(\mu_3-\eta^2-CF_3N{\equiv}C)$[11] adopt an almost superimposable $Fe_3(RN{\equiv}C)$ core structure. In all five cases the C−N bond length varies only from 1.26 to 1.31 Å and the maximum deviation between corresponding Fe−N resp. Fe−C bonds is 0.10 Å. All this is in accord with the description of the capping ligand as a σ-donor towards Fe2 and a twofold π-donor towards Fe1 and Fe3.

Figure 1. Molecular structure of **5a**



Pertinent distances [Å]: Fe1−Fe2 2.627(1), Fe1−Fe3 2.487(1), Fe2−Fe3 2.646(1), Fe1−C7 1.998(4), Fe3−C7 2.087(4), Fe1−N1 1.976(3), Fe3−N1 1.956(3), Fe2−N1 1.779(3), Fe2−P1 2.154(1), N1−C7 1.290(5). Selected angles [°]: Fe1−Fe2−P1 152.0(1), Fe2−N1−C7 158.4(3), N1−C7−C6 132.7(4).

The attachment of the phosphite ligand causes minor deviations of the symmetry of the Fe_3CN core. The most visible one of these is the difference in the Fe−C7 bond lengths. The bond length of Fe3−C7 is 0.09 Å longer than that of Fe1−C7, indicating some repulsive interactions between the phosphite and the nitrile ligands. The phosphorus atom, as usual[12], is attached equatorially. It is placed above the Fe_3 plane like its neighboring CO ligands 21, 31, and 11 with a dihedral angle P1Fe2Fe3/Fe1Fe2Fe3 of 158°. The presence of the phosphite ligand causes a shortening effect (0.02−0.03 Å) on all bonds from iron to the nitrile ligand as compared to **2a**. This may reflect the enhanced stability of **5a**.

Altogether this paper has shown that the yields of the parent cluster **2** and its derivatives can be moderately improved and that enhanced stability is achieved with electron-withdrawing substituents on the capping nitrile or by replacement of CO by trimethyl phosphite. It now remains to be shown that the capping nitrile is a synthon which is susceptible to variations of the known hydrogenation/dehydrogenation sequences.

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Experimental

All general procedures and the instruments used were as described before[13]. Starting materials were obtained commercially. Silica gel (Macherey-Nagel, Kieselgel 60, 0.063–0.2 mm and Merck, Kieselgel 60-F_{254}, 0.25-mm layer) was used for column and thin-layer chromatography. Analytically pure compounds are characterized in Table 6.

Preparation of the Clusters **2**: 0.5–2.5 g of $Fe_3(CO)_{12}$ and an excess of the nitrile were dissolved in 100–200 ml of cyclohexane. Hydrogen was bubbled through the solution for the whole reaction time. The mixture was heated at reflux until TLC indicated that all $Fe_3(CO)_{12}$ had been consumed. Then the solvent was removed in vacuo, the residue taken up in dichloromethane, the solution filtered through silica gel and evaporated to drynes. Except for **2j** and **k**, which were isolated by preparative TLC, the clusters **2** were isolated by column chromatography using hexane and then hexane containing increasing amounts of CH_2Cl_2 as eluent. The first fraction contained remaining $Fe_3(CO)_{12}$ (green), the second fraction the corresponding cluster **2** (brown). All details of the preparations are given in Table 4.

Table 4. Reaction conditions for clusters **2**

$Fe_3(CO)_{12}$ g	mmol		nitrile mg	mmol	cycloh. ml	time h		product mg	%
9.75	19.3	**1a**	2000	19.4	500	4	**2a**	3500	35
1.03	2.05	**1b**	240	2.05	150	5	**2b**	150	14
1.00	1.99	**1c**	288	1.97	100	1.5	**2c**	68	6
1.00	1.99	**1d**	263	1.96	100	1	**2d**	230	21
0.87	1.73	**1e**	300	2.34	100	2	**2e**	78	8
0.72	1.42	**1f**	187	1.46	75	4	**2f**	27	4
0.85	1.69	**1g**	289	2.26	100	3.5	**2g**	67	7
1.30	2.58	**1h**	450	2.63	75	3	**2h**	184	13
2.00	3.97	**1i**	860	4.46	175	4	**2i**	500	21
1.00	1.99	**1j**	195	1.88	100	4	**2j**	traces	
1.00	1.99	**1k**	288	2.76	100	3	**2k**	traces	

Isonitrile Derivatives **3**: 580 mg (1.10 mmol) of **2a** and 125 mg (1.00 mmol) of *p*-tolyl isocyanide in 75 ml of CH_2Cl_2 were stirred for 20 h. The volume was reduced in vacuo to 5 ml and the solution filtered through silica gel. Then the solvent was removed and the residue chromatographed with hexane/CH_2Cl_2 (9:1) over a 3 × 15 cm column. The first fraction (brown) contained 50 mg of unreacted **2a**, the second fraction (brown) yielded 35 mg (6%) of **3a**.

4a: Isolated by the same procedure from 280 mg (0.54 mmol) of **2a** and 53 mg (0.64 mmol) of *tert*-butyl isonitrile in 35 ml of cyclohexane for 24 h. Yield 30 mg (10%).

Phosphane Derivatives: The starting cluster was dissolved in dichloromethane and the phosphane added to the solution. After stirring at the appropriate temperature until TLC indicated that the concentration of the starting cluster was constant, the solvent was removed in vacuo and the residue chromatographed with hexane/CH_2Cl_2 (1:1). The first fractions contained traces of $Fe_3(CO)_{12}$ (green) and some unreacted cluster **2** (brown). The next fraction (brown) contained the product which in the case of **5a** and **i** was followed by green fractions of $Fe_3(CO)_{10}[P(OMe)_3]_2$ and $Fe_3(CO)_9[P(OMe)_3]_3$. Table 5 lists the details.

Structure Determination[14]: Brown crystals of **5a** were obtained by cooling a hexane solution to −30°C: $C_{18}H_{14}Fe_3NO_{11}P$, mol. wt. 618.8, crystal size 0.15 × 0.3 × 0.7 mm, space group $P2_1/c$, $Z = 4$, $a = 9.336(2)$, $b = 9.663(2)$, $c = 27.415(5)$ Å, $\beta = 97.78(3)°$, $V = 2450.4(9)$ Å^3, $d_{calcd.} = 1.68$, $d_{obsd.} = 1.69$ gcm^{-3}, $\mu = 18.7$ cm^{-1}, 2Θ range 2–43°, hkl range $\pm h$, $+k$, $+l$, 2827 independent reflections with $I \geq 3\sigma(I)$, 295 variables, $R = 0.032$, residual electron density maxima +0.3 and −0.4 e/Å^3. The data were obtained by using a Nonius CAD4 diffractometer with Mo-K_α radiation ($\omega/2\Theta$ technique). The structure was solved by means of direct methods and refined anisotropically after an empirical absorption correction[15]. Hydrogen atoms were included on fixed positions by application of a common isotropic temperature factor. Computations were carried out by employing the PC version of SHELX[16]. The drawing was obtained by means of the SCHAKAL program[17].

Table 5. Reaction conditions for phosphine substitutions

	cluster mg	mmol	phosphane	mg	mmol	CH_2Cl_2 ml	°C	time h		product mg	%
2a	527	1.00	$P(OMe)_3$	112	0.90	30	25	5	**5a**	102	16
2i	260	0.42	$P(OMe)_3$	32	0.25	70	40	3.5	**5i**	40	13
2i	240	0.39	PPh_3	62	0.24	70	40	3.5	**6i**	170	85
2a	113	0.22	dppe	83	0.22	45	25	3	**7a**	20	11
2i	38	0.06	dppe	23	0.06	12	25	17	**7i**	53	94

Table 6. Analytical characterizations

Nr.	formula (mol. wt.)	m.p. °C		analyses C	H	N
2b	$C_{17}H_7Fe_3NO_9$	88	calc.:	38.04	1.31	2.61
	(536.8)		found:	37.60	1.35	2.42
2d	$C_{17}H_7Fe_3NO_{10}$	109	calc.:	36.94	1.28	2.53
	(552.8)		found:	37.05	1.45	2.51
2e	$C_{17}H_4Fe_3N_2O_9$	121	calc.:	37.28	0.74	5.11
	(547.8)		found:	37.40	1.02	4.81
2f	$C_{17}H_4Fe_3N_2O_9$	113	calc.:	37.28	0.74	5.11
	(547.8)		found:	36.76	0.76	5.05
2i	$C_{16}F_5Fe_3NO_9$	146	calc.:	31.36	--	2.28
	(612.7)		found:	31.13	--	2.21
5i	$C_{18}H_9F_5Fe_3NO_{11}P$	127	calc.:	30.50	1.28	1.98
	(708.8)		found:	30.80	1.76	1.85
6i	$C_{33}H_{15}F_5Fe_3NO_8P$	122	calc.:	46.80	1.79	1.65
	(847.0)		found:	47.43	1.55	1.75
7a	$C_{39}H_{27}Fe_3NP_2O_7$	114	calc.:	55.04	3.20	1.65
	(851.1)		found:	55.27	3.31	1.43
7i	$C_{39}H_{22}F_5Fe_3NO_7P_2$	148	calc.:	49.78	2.36	1.49
	(941.1)		found:	49.40	2.50	1.44

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[14] Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, giving reference to the depository number CSD-401756 and citing the authors and this paper.

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