Ab Initio Study of Bonding Trends among Cyanamidophosphates ($[PO_n(NCN)_{4-n}]^{3-}$) and Related Systems

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Abstract: Ab initio calculations on the experimentally known anions $[PO_n(NCN)_{4-n}]^{3-}$ are used to show that intramolecular forces are sufficient to determine their existence and structure. Structures are predicted for the analogous cyanamidosulphates and perchlorates. If one of the oxygens of the $XO_4{}^q$ group is replaced by nitrogen or fluorine, further new anions are obtained. An example is $NSO_3{}^{3-}$. Remarkably, the $NArO_3{}^-$ anion is predicted to have strong inner bonding and is, together with ArO_4, a candidate for an argon species.

Keywords: ab initio calculations • cyanamide • oxygen • phosphates • pseudochalcogens • sulphates

Introduction

New, simple inorganic species can still be found. Predictions for them can be obtained from ab initio calculations for systematic, isoelectronic sequences. Furthermore, the pseudohalogen or pseudochalcogen concepts provide useful ways of thinking on possible extensions. We have already carried out such studies for multiply bonded chains, from diatomic to penta-atomic ones,[1] and several of the predicted species, notably $N_5{}^+$[2, 3] and $OCNCO^+$[4] have later been synthesized as ions in the solid state.

We consider here two such series. The sulphate isoelectronic series $PO_4{}^{3-}$, $SO_4{}^{2-}$, $ClO_4{}^-$ has already been expanded up to ArO_4[5] and the high-lying local minimum has survived later theoretical scrutiny.[6] We now consider a number of lower symmetry systems in which one O atom is replaced by the isoelectronic N^- or F^+. Four such species, $NClO_3{}^{2-}$, $FPO_3{}^{2-}$, $FSO_4{}^-$ and $FClO_3$, are experimentally known and more may exist.

Secondly we consider the substitution of the O atoms in these tetrahedral groups by one particular pseudochalcogen, namely cyanamide, NCN.[7] The entire series of such substitutions, $[PO_{4-n}(NCN)_n]^{3-}$ ($n = 0-4$) was achieved[7–11] notably by the late Helmut Köhler,[12] but little structural information and no previous ab initio studies exist. This substitution would also seem to have considerable potential for extension. For the latest review on pseudochalcogens, see ref. [10].

Results and Discussion

The $XO_4{}^q$ series: These geometries are given in Table 1. It is seen that both the calculated and the experimental X–O bond lengths decrease along the series X = P, S, Cl, (Ar). Lindh et al.[6] found a bond-length minimum at X = Cl and obtained a value of 1246 kJ mol^{-1} for the heat of formation of argon tetroxide.

Fluorine substitution: Several species, obtained by substitution of one oxygen by a neighbouring atom, are included in Table 1. A complete map of the possible species with 3rd-row X and 2nd-row Y is shown in Figure 1. The trends of the X–O and X–N bond lengths are shown in Figures 2 and 3, respectively, as function of the central atom X. The structures of the $FXO_3{}^q$ species can be compared with experimental data in three cases. There are crystal data for several compounds of monofluorophosphate, $FPO_3{}^{2-}$.[16] Note that the F–X bond lengths are longer than the X–O ones. Numerous compounds of fluorosulphate, $FSO_3{}^-$, are also known.[21] As the sum of the F and S covalent radii[23] is 64 + 104 = 168 pm, the F–S bond has little multiple character. The third case is gaseous $FClO_3$, a very stable compound.[24] As seen from Table 1, the agreement between theory and experiment is good and it is improved by the larger basis set b (see Computational Methods).

The vibrational frequencies of the $FXO_3{}^q$ species are given in Table 2. A large amount of data exist for fluorosulphate compounds. The present calculations support the experimental assignments in refs. [21, 29, 30] The comparison with the gas-phase spectra of $FClO_3$ is also very satisfactory. The agreement with the experimental assignment of Kirillov et al.[26] for monofluorophosphate is also acceptable, while that with Nelson and Williamson[28] is less clear.

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Table 1. Optimized geometries for the penta-atomic species Y_nXO_{4-n}. Bond lengths in picometers, angles in degrees. MP2 level, unless otherwise stated.

Species	Basis set[a]	X−O	X−Y	Y−X−O	Comments
SiO_4^{4-}	a	173.0	173.0		
		162	162		expt[13]
PO_4^{3-}	a	160.0	160.0		
		151	151		expt[13]
SO_4^{2-}	a	152.2	152.2		
		149	149		expt[13]
ClO_4^-	a	148.3	148.3		
	b	146.6	146.6		CCSD(T)
		143	143		expt[13]
ArO_4	a	147.7	147.7		this work and ref. [5]
	b	144.6	144.6		
	a	156.0	156.0		CCSD(T)
	b	149.6	149.6		CCSD(T)
		147.6	147.6		BCCD(T)/ANO[6]
NPO_3^{4-}	a	168.3	163.4	114.93	
NSO_3^{3-}	a	159.6	152.8	114.95	
$NClO_3^{2-}$	a	156.1	146.6	115.04	
		average 153(7)		expt[14]	
$NArO^{3-}$	a	157.2	144.0	115.25	
	a	168.2	151.2	115.28	CCSD(T)
	b	153.3	142.3	115.22	
	b	160.2	146.2	115.25	CCSD(T)
FPO_3^{2-}	a	154.0	171.9	101.87	
	b	152.8	170.9	101.84	
		150.9	158.7	104.45	HF[15]
		150	157		expt[16]
		149.3	160.6	103.1	expt[b]
FSO_3^-	a	147.1	166.8	101.98	
	b	145.6	164.5	102.0	
	a	143.6	160.2	102.4	HF[18, 19]
	TZV	147.1	168.9	101.80	ECP-QCISD(T)[20]
		144	157	106	expt[c]
$FClO_3$	a	144.3	168.5	101.89	
	b	141.8	164.9	101.85	
		140.4(2)	161.9(4)	100.8	expt[22]
$FArO_3^+$	a	144.9	177.1	101.62	
	b	141.9	172.6	101.36	
$NeClO_3^+$	b	143.2	284.4	90.07	
WO_4^{2-}	a		175.6		
			170-		expt[13]

[a] a = 6−31g* basis set, b = cc-pVTZ basis set. [b] In β-Na_2PO_3F (average).[17] [c] In $CsSO_3F$ (average).[21]

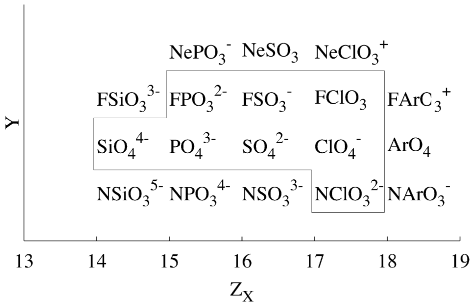

Figure 1. A complete map of the YXO_3^q species with 2nd-row ligands, Y, and 3rd-row central atoms, X. The "island of stability" of experimentally known species is framed.

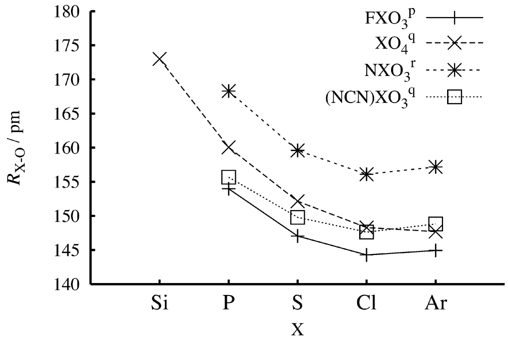

Figure 2. The trends of the calculated X−O bond lengths at the MP2/6-31g* level for the species indicated. X is the central atom.

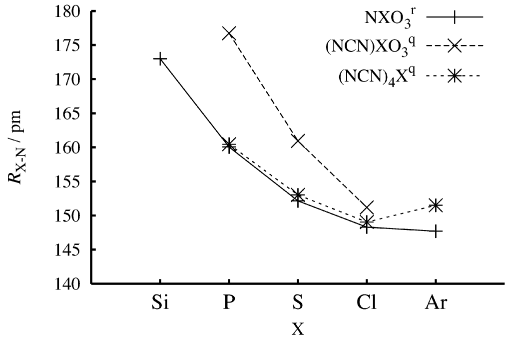

Figure 3. The trends of the calculated X−N bond lengths at the MP2/6-31g* level for the species indicated. X is the central atom.

If more than one oxygen atom is substituted by fluorine, one obtains, for instance, the valence isoelectronic series $FClO_3$, F_2SO_2, F_3PO, F_4Si used by Lindh et al.[6] for discussing the heats of formation.

Abstract in Finnish: *Anionisarjalle* $[PO_n(NCN)_{4-n}]^{3-}$ *suoritetut kvanttikemialliset ab initio-laskut osoittavat molekyylinsisäisten voimien riittävän selittämään näiden kokeellisesti tunnettujen anionien olemassaolon ja rakenteen. Analogisten syanamidosulfaattien ja perkloraattien kokeellisesti tuntemattomat rakenteet on myös laskettu. Mahdollisia uusia anioneja saadaan myös korvaamalla* XO_4^q*-ryhmien happiatomi typellä tai fluorilla. Esimerkki tällaisesta ionista olisi* NSO_3^{3-}*. Yllättäen tämä trendi jatkuu jalokaasu argoniin asti; anionilla* $NArO_3^-$ *on voimakkaat sisäiset sidokset. Aiemmin ehdotetun argontetroksidin ohella se tarjoaa uusia mahdollisuuksia valmistaa ensimmäinen kiinteän olomuodon argonyhdiste.*

Nitrogen substitution: In contrast with fluorine substitution, if one oxygen is replaced by N^-, the resulting N−S bond length is *shorter* than the S−O one and much shorter than the sum of (single) covalent radii, 70 + 104 = 174 pm. At the same time the remaining X−O bond becomes longer compared with the tetrahedral XO_4^q case.

The only experimentally known member of the nitrogen-substituted, NXO_3^q species is the perchlorylimide anion, $NClO_3^{2-}$. Its thermally stable but explosive potassium salt was reported in 1958.[31] The infrared spectrum of this potassium salt has been reported,[25] see Table 2. The agreement with the calculated frequencies is excellent for the higher frequencies. The doubts of Karelin et al.[25] on their assignment of the lower frequencies are also supported by the

Table 2. Calculated vibrational frequencies [cm^{-1}] for the YXO_3^q species. MP2 unless otherwise stated. No scaling factors were applied. Note that in the tetrahedral case of ArO_4 $t_2 = e + a_1$. The calculated IR intensities [km mol^{-1}] are given in brackets.

Species	Basis set[a]	e	e	a_1	a_1	e	a_1	Comments
			t_2			t_2		
NSO_3^{3-}	a	417	562	596	819[e]	902	1192[f]	
$NClO_3^{2-}$	a	420	563	599	833	922	1313[f]	
		[0.09]	[9.6]	[17]	[127]	[426]	[343]	
		(625)	(597)	(597)	829	893	1267	expt[b]
$NArO_3-$	a	385	522	550	754[e]	859	1357[f]	
	a	291	384	393	450	597	976	CCSD(T)
	b	419	550	581	805	877	1335[f]	
$OArO_3$	a	399	573	573	955	1098	1098	
	a	308	444	444	587	801	801	CCSD(T)
	b	439	608	608	996	1148	1148	
	b				680			CCSD(T)
		477	377	377	725	918	918	large-basis BCCD(T)[c]
FPO_3^{2-}	a	347	526	494	678[f]	1181	966[e]	
		380	530	713–795	1000	1130–1230	expt[g]	
		379	520	520	795[f]	1136	1002[e]	expt[h]
FSO_3^-	a	372	529	561	743	1328	1071	
						1412	1161	HF[19]
		410	584	563	743	1272	1083	expt[i]
$FClO_3$	a	362	548	507	710	1360	1104	
	b	391	576	533	693[f]	1383	1116[e]	
		405	589	549	715	1315	1061	expt[d]
$FArO_3^+$	a	293	489	442	611[f]	1308	1114	
	b	340	526	474	614[f]	1347	1120	

[a] a = 6–31g*, b = cc-pVTZ. [b] In $K_2(NClO_3)$.[25] Assignments in parentheses uncertain. [c] BCCD(T) results from ref. [6]. [d] Ref. [27]. [e] X–O stretch. [f] X–Y stretch. [g] In solid Na_2PO_3F and in aqueous solution.[28] [h] Ref. [26]. [i] In solid $(NF_4)(FSO_3)$ (averaged).[29]

present calculations. Note that the calculated intensity of the lowest e vibration (see Table 2) is very small so it may have been missed in the experiment.[25] The structures of the K, Sr and Ba salts of this anion and of $CaNClO_3 \cdot nH_2O$ have been studied, but only an average of 153(7) pm for the Cl–N and Cl–O bond lengths is reported.[14] At high temperatures (above 360 °C), the predominant disintegration reaction of $BaNClO_3$ is the solid-state one [Eq. (1)].[32]

$$2\,BaNClO_3 \longrightarrow Ba(NO_3)_2 + BaCl_2 \qquad (1)$$

The other nitrogen-containing species appear to be so far unknown. A conspicuous fingerprint for them would again be the X–N and X–O stretch vibrations. Perhaps the best candidate would be the nitridosulphate $[NSO_3]^{3-}$. The nitridotrisulphate, $[N(SO_3)_3]^{3-}$, and imidodisulphate, $[HN(SO_3)_2]^{2-}$, are known.[24] The nitridosulphate also could be seen as deprotonated sulphamate, $[H_2NSO_3]^-$. As the sulphamic acid is a strong acid, further deprotonation of its anion may be possible.

Argon compounds: Argon compounds in bulk are so far unknown, apart from clathrates. In addition to the previously studied ArO_4,[5, 6] we here find short bond lengths and clearly positive vibrational frequencies (see Table 1 and Table 2) for the $NArO_3^-$ anion. It could possibly be made by firing neutral or ionized argon at crystalline nitrates or frozen nitrate solutions, followed by subsequent sputtering or thawing, or possibly in situ observation. For the anions, this would be the inverse of reaction given in Equation (1). The energies for such a purely hypothetical $Ar + NO_3^-$ symmetrical reaction path are shown in Figure 4. It suggests that about 1 au of energy is needed to pass the head-on barrier between the two minima and that the higher lying minimum would be about 0.2 au below that maximum. The calculated MP2/cc-pVTZ energy of $NArO_3^-$ lies 0.66545 au above $Ar + NO_3^-$.

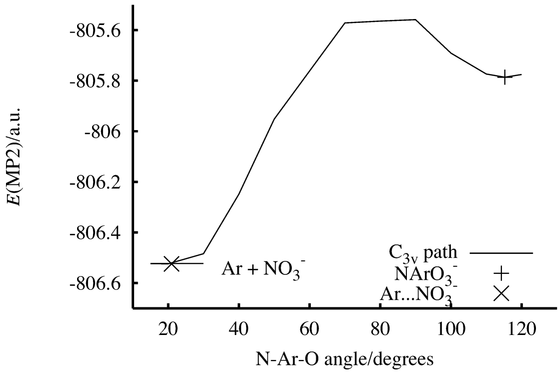

Figure 4. The calculated MP2/6-31g* energies for an $Ar-NO_3^-$ system as function of the N-Ar-O angle along the path with C_{3v} symmetry. The weak complex between an argon atom and nitrate is on the left-hand side and the quasitetrahedral $NArO_3^-$ on the right-hand side.

A further risk for the existence of $NArO_3^-$ would be the triplet states. Exploratory HF-level calculations show the triplet to lie 0.15 and 0.13 au above the singlet for cc-pVTZ and 6-31g* basis sets, respectively, at their MP2 geometries. Anyway, as discussed in the case of N_5^+,[1] the crystal field can stabilize the singlet state, even if it were higher than the triplet state for the free ion. Note that the $NArO_3^-$ anion only contains "air".

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The other new argon-containing molecule, $FArO_3^+$, is a local minimum at the MP2 level with both basis sets a and b (see Computational Methods), but disintegrates at CCSD(T)/6-31g* level. For $NeClO_3^+$, only a weak complex with a long NeCl distance of 284 pm was found.

Highly ionized argon species, such as Ar_2N^{2+}, have been discussed theoretically, as well as the monocations $ArCN^+$ and $ArCCH^+$.[33] The diatomic ArN^+ ($X^3\Sigma^-$, $D_0 = 2.16(10)$ eV) has been observed experimentally.[34, 35] However, the present neutral or anionic, polyatomic argon nitride species with short and strong Ar–N bonds seem to be new. In addition to the sulphate isoelectronic analogues, the SO_2 analogue ArN_2 and the SO_3 analogues $OArN_2$ and ArN_3^- present themselves. All are local minima at the lower MP2 level of theory. At the higher CCSD(T)/cc-pVTZ level only the last survives, see Table 3. The energy of ArN_3^- lies 0.6900 and 0.6893 au above $Ar + N_3^-$ at the two levels, respectively. Recall the 0.6654 au at MP2 level for $NArO_3^-$ compared with $Ar + NO_3^-$.

Cyanamide substitution: After this preamble we now discuss the title compounds. The calculated structures of the species, in which one or more O atoms are replaced by NCN groups, are given in Table 4 and their X–O and X–N bond lengths are included in Figure 2 and Figure 3. The vibrational frequencies of cyanamidophosphate are given in Table 5. A first observation drawn from Figure 2 is that the X–O bond lengths of the NCN-substituted species pass from the fluorine-substituted curve to the all-oxygen curve for increasing Z_X. Thus one could surmise that, as a ligand, cyanamide should be placed between fluorine and oxygen. Support for this proximity of cyanamide and oxygen is obtained from the ESCA (electron spectroscopy for chemical analysis) spectra of the sodium and

Table 3. Results for three- and four-atom argon species. A cc-pVTZ basis is used. Bond lengths in pm, angles in degrees, frequencies in cm^{-1}.

System	Symmetry	Method	Ar–N	Ar–O	Angle	Comments
ArN_2	C_{2v}	MP2	158.4	–	136.9[a]	
		CCSD(T)	> 186	–	168	breaks up
$OArN_2$	C_{2v}	MP2	153.0	153.8	112.86[b]	a_1 414, 728, 919, b_1 440, b_2 520, 1034
		CCSD(T)	> 207	186	122	breaks up
ArN_3 –	D_{3h}	MP2	156.6	–	(120)[a]	a_1' 704, a_2'' 466, e' 463, 1088
		CCSD(T)	162.7	–	–	–

[a] N-Ar-N. [b] O-Ar-N.

Table 4. Optimized MP2 geometries for the $O_3X(N_1CN_2)$ and $X(N_1CN_2)_4$ species.

System	Basis set	X–O	X–N_1	N_1–C	C–N_2	O–X–N	Comments
$O_3P(NCN)^{3-}$	a	155.7	176.7	125.3	124.6	105.16	C_{3v} assumed
	a	155.9	179.8	127.7	123.7	102.2	C_s assumed
	b	154.7	178.6	126.4	123.0	102.44	C_s assumed
						2 × 106.66	
		151.7 – 152.8	167.2	129.2	117.4	104.2	expt[11][b]
$O_3S(NCN)^{2-}$	a	149.8	160.9	126.1	122.0	106.98	C_{3v} assumed
	a	149.6	167.8	130.9	120.9	103.04	C_s assumed
		2 × 150.1				2 × 112.2	
	b	148.0,	167.0	129.8	120.0	103.05,	C_s assumed
		2 × 148.3				2 × 108.52	
$O_3Cl(NCN)^-$	a	147.6	151.2	128.2	120.0	108.77	C_{3v} assumed
	a	146.7	164.1	134.0	119.4	102.77	C_s assumed
		2 × 147.7				2 × 110.29	
	b	144.2,	162.2	133.0	118.3	102.91	C_s assumed
		2 × 145.1				2 × 110.11	
$O_3Ar(NCN)$	a	148.8	145.5	131.2	119.2	110.70	C_{3v} assumed
	b						C_s N–Ar bond breaks
$O_3W(NCN)^{2-}$	a	173.9	184.0	128.2	121.3	110.09	C_{3v} assumed
$P(NCN)_4^{3-}$	a		160.4	126.7	121.6		T_d assumed
$S(NCN)_4^{2-}$	a		153.0	127.7	120.4		T_d assumed
$Cl(NCN)_4^-$	a		149.0	129.2	119.7		T_d assumed
$Ar(NCN)_4$	a		151.5	130.7	120.1		T_d assumed

[a] a = 6 – 31g*, b = cc-pVTZ. [b] In $Na_3PO_3NCN \cdot 7H_2O$, expt N-C-N angle 175.2°.

Table 5. Calculated MP2/6 – 31g* frequencies [cm^{-1}] for $(NCN)XO_3^q$ for the C_s structure in Figure 5b.

X		Low frequency	High frequency
P	calcd	21, 116, 338, 340, 416, 518, 520, 603, 615, 686	926[b], 1113, 1113[b], 1279[c], 2250[d]
	expt[a]	620, 722, 794,	975[b], 1061[b], 1276[c], 2150[d]
S	calcd	40, 151, 379, 385, 487, 548, 556, 586, 655, 781	1022, 1203, 1214, 1238, 2137
	expt[e]	600, 610, 805	1120, 1240[c], 1370[b], 2150[d]
Cl	calcd	59, 159, 367, 388, 470, 517, 543, 558, 658, 764	1042, 1137, 1192, 1224, 2180

[a] In $Na_3PO_3NCN \cdot 7H_2O$.[36] [b] $\nu(X{=}O)$. [c] $\nu_s(NCN)$. [d] $\nu_{as}(NCN)$. [e] In $Na_2[SO_3(NCN)] \cdot 2H_2O$.[37]

silver cyanamidophosphates.[38] The decreasing electronic charge of the individual cyanamides upon increasing substitution, n, was noticed in a CNDO interpretation of these ESCA spectra of sodium cyanamidophosphates ($n = 0-4$).[39]

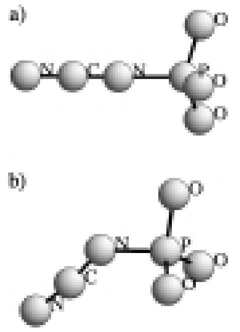

Figure 5. The calculated MP2/6-31g* structures of $O_3P(NCN)^{3-}$ assuming a) C_{3v} or b) C_s symmetry.

A detail that should be mentioned is that the C_{3v} species (Figure 5a) have an imaginary e vibrational frequency that becomes real when the system is bent to C_s symmetry (Figure 5b). The resulting energy change is very small, −0.00513 au for $(NCN)PO_3^{3-}$ at the MP2/6-31g* level. Therefore, the system is very floppy and the crystal forces could easily "wag" or straighten the NCN tail. The experimental OPO and OPN angles in solids are nearly tetrahedral.[11] The P–N bond length in solids (167.2 pm) is somewhat shorter than the calculated one at MP2/6-31g* level (177 pm) without any counterion effects. The experimental P–N bond length was taken as evidence for a bond order of about 1.5.[11] The interesting aspect about the bonding in the title species is the cumulated chain of multiple bonds in the X=N=C=N chain.

At this point it is interesting to quote the experimental, bent cumulene structure of $Ph_3P{=}C{=}C{=}X$, X = O,S. The bond angle at C is 145.5° and 168° for ketene and thioketene, respectively. Notice the large variation. The C–C and C–O bond lengths are 121.0 and 118.5 pm, respectively.[40] Thus the two pseudochalcogens, cyanamide and (thio)ketene, exhibit similar bonding to four-coordinated P^V. For X = P, which has the longest X–N bond length, the two N–C bond lengths inside the cyanamide are still almost equal. As the $X{-}N_1$ bond length decreases, the nearest $N_1{-}C$ bond length grows and the peripheral $C{-}N_2$ bond length shrinks, see Table 3. The more strongly the cyanamide bonds to the central atom X, the more it distorts itself. The $X(NCN)_4^q$ species have shorter X–N bond lengths than the monosubstituted species. Apart from the substituted phosphates, all of which are known, the sodium salts of mono- and dicyanamidosulphates, and their IR spectra have been reported.[37] None of the other systems in Table 4 seem to be known. Perhaps the best candidates for new species would be the nearest neighbours, that is, the corresponding perchlorates, $[ClO_n(NCN)_{4-n}]^-$. Finally it should be said that oxygens in many other groups can be replaced by cyanamide. Some examples are cyanate ($CNO^- \rightarrow NCNCN^-$), carbonate ($CO_3^{2-} \rightarrow CO(NCN)_2^{2-}$), nitrate ($O_2N(NCN)^-$, see ref. [41]), carboxylate ($RCO_2^- \rightarrow RC(O)NCN^-$) and sulphonate ($RSO_3^- \rightarrow RSO_2NCN^-$). All of these have been quoted by Köhler et al.[9, 10]

Substituted oxotungstates: The exploratory calculation on the monosubstituted tetraoxotungstate, $(NCN)WO_3^{2-}$ reveals a stable C_{3v} geometry; this is in contrast to the main-group oxoanions, which tend to bend.

Substituted uranyl: One oxygen of the uranyl ion, OUO^{2+}, could be replaced by an NCN group at Hartree–Fock level, see Table 6. The U–N bond length of 172.3 pm is longer than the U–O one of 162.8 pm, and the latter is shortened from the uranyl value of 163.6 pm. This monosubstituted uranyl, $OUNCN^{2+}$, is linear.

Table 6. Calculated bond lengths for uranyls [pm].

System	U–O	U–N	Comments
OUO^{2+}	163.6	–	HF
$OU(NCN)^{2+}$	162.8	172.3	HF
OUN^+	169.0	161.5	HF
	176.1	172.5	MP2

This effect of the NCN substitution on the remaining U–O bond length is similar to that in Figure 2, and again suggests that cyanamide is more electronegative than oxygen itself. Recall that the nitride (N) substitution has the opposite effect, both in Figure 2 and in the triatomic OUN^+ predicted in ref. [42] and prepared in ref. [43].

The limits of the pseudochalcogen analogy: The limits of the pseudochalcogen analogy become evident if further cyanamide analogues of common oxygen compounds are considered.

The oxygen molecule, O_2, would have as its analogue an $(NCN)_2$ molecule. This molecule actually reorganizes itself to a *trans*-dicarbonitrile N≡C–N=N–C≡N. Its infrared spectrum is experimentally known[44] and is compared with calculated ones in Table 7. Note that while O_2 has a $\pi_x^1\pi_y^1\,{}^3\Sigma$ ground state, the non-linear $(NCN)_2$ has a singlet ground state. The calculated N≡C, C–N and N=N bond lengths are 118.8, 137.4 and 128.9 pm, respectively, and the C-N-C angle 111.41°.

Similarly, the analogue of the linear carbon dioxide, O=C=O, becomes the bent, *trans* N≡C–(N=C=N)–C≡N, with N≡C, C–N and N=C bond lengths of 118.8, 133.4 and 122.8 pm, respectively, at MP2/6-31g* level. The dihedral angle of the C_2 structure is 95.19°, the C-N-C angle is 135.59°. If only one oxygen is substituted, we obtain the planar NCNCO, which again is both experimentally and theoretically known.[46, 45]

The analogue of carbon monooxide (C)O is CNCN, an experimentally known, linear isomer of cyanogen.[47] The "water" analogue H–(NCN)–H is the known carbodiimide form of cyanamide.

Table 7. Calculated MP2/6–31g* and experimental[44] IR frequencies for *trans*-azodicarbonitrile, N≡C–N=N–C≡N.

	a_u	b_u	a_g	b_g	a_g	a_u	b_u	b_u	a_g	a_g	a_g	b_u
calcd	125	138	266	352	564	572	583	999	1037	1400	2139	2164
expt[a]	133	b_g 108	282	–	741	574	596	904, 982	1002	1422	2176	2204

[a] Ref. [44].

Conclusion

1. The present calculations support the interpretation of the title species $[PO_n(NCN)_{4-n}]^{3-}$ as phosphates in which the oxygens are substituted by the pseudochalcogen cyanamide. The calculated structure of the free $[PO_3(NCN)]^{3-}$ anion resembles that in the one known crystal structure. The −NCN tail is very floppy. Both the short P–N bond and the vibrational spectra are reproduced.
2. The electronegativity of the cyanamide group is between that of fluorine and oxygen itself.
3. The analogous cyanamidosilicates or -perchlorates seem to be unknown. Two cyanamidosulphates are known, but only the vibrational spectra are available. The structures for these three ions are predicted.
4. If one oxygen atom in the $XO_4{}^q$ is replaced by a single-atom substituent, namely F or N, a number of penta-atomic species $YXO_3{}^q$ is obtained. Eight of them are already known, including the four tetrahedral ones. The possible new species include $NSO_3{}^{3-}$, $NArO_3{}^-$ and the previously theoretically studied ArO_4.
5. Among other high-energy argon nitride species considered, the $ArN_3{}^-$ anion is bound at all levels of approximation.
6. The limits of the picture of NCN as a pseudo-oxygen atom are studied in a number of simple cases and these analogues sometimes correspond to already known compounds.

Computational Methods

The Gaussian 98 package[48] was used. The lighter elements were treated by using the 6-31g* or cc-pVTZ basis sets. The 14-valence-electron (VE) quasi-relativistic (QR) pseudopotential (PP) of Andrae[49] was used for W. One f-type polarisation function[50] was added. Uranium was handled by using the 14-VE PP of Hay et al.[51]

The basis-set convergence can be tested on ArO_4 at the CCSD(T) level against the results of Lindh et al.[6] We used two basis sets with a) double-zeta plus polarization and b) triple-zeta. For the third-row elements like argon, these correspond to (4s3p1d) and (5s4p2d1f), respectively. Lindh et al. used a (5s4p3d2f) "ANO" basis set. From Tables 1 and 2 it is seen how the present results approach those of Lindh et al.

Many of the present species carry large negative charges ($q < -1$). We tried to model them in condensed matter, in which all occupied orbitals are bound. Therefore normal basis sets (without the diffuse functions needed to treat gas-phase anions) are appropriate. The quantitative deviations of such free-anion calculations from structural data for crystals have been discussed by Pyykkö and Zhao.[52] It was concluded that for anions with strong multiple bonds (e.g., the triatomic A=B=C series including cyanamide, NCN^{2-}), the results remain close to experiment down to about $q = -4$. The systems with weaker internal bonds distort or dissociate much earlier.

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