Supplementary information for:

The complete conformational panorama of formanilide-water complexes: the role of water as conformational switch.

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Abstract

The microsolvated complexes of formanilide, generated in a supersonic expansion, have been observed by Fourier transform microwave spectroscopy. Three 1:1 and one 1:2 formanilide-water adducts have been observed and their structure characterized by the measurement of isotopologue rotational spectra. In one of the monohydrated complexes and in the dihydrated complex formanilide adopts a *cis*-configuration. In these species water closes sequential cycles with the *cis* amino and carbonyl groups through a network of N-H···O and O-H···O hydrogen bonds. Furthermore, in these complexes *cis*-formanilide has almost the same non planar configuration observed in the monomer. In the two monohydrated complexes detected with *trans*-formanilide, a planar skeleton is detected with water interacting solely with either the amino (N-H··O bond) or the carbonyl group (O-H···O=C bond). The observed tunnelling splittings show a rich intermolecular dynamics in those complexes. The results seem to indicate that complexation with water switches the configuration of formanilide from *trans*, more stable for the bare monomer, to *cis*, more stable for the hydrated complexes.

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Figure S1. Monohydrated complexes for the *cis* and *trans* configurations of formanilide with labeling and relative energies respect to the most stable complex (*cis*-fa-w-a) at the MP2/6-311++G(2d,p) level of theory. Black dashed lines indicate the interactions established through hydrogen bonds [Ref. 23].

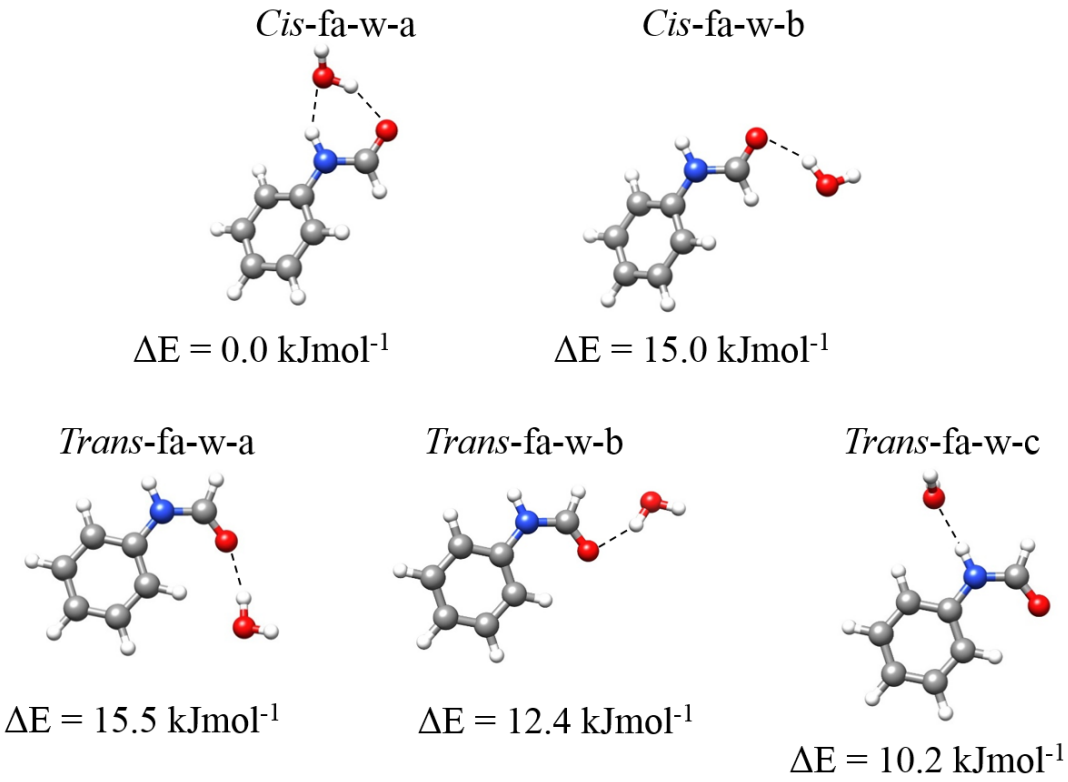


Figure S2. Dihydrated complexes for the *cis* and *trans* configurations of formanilide with labeling and relative energies respect to the most stable complex (*cis*-fa-w_2-a) at the MP2/6-311++G(2d,p) level of theory. Black dashed lines indicate the interactions established through hydrogen bonds [Ref. 23].

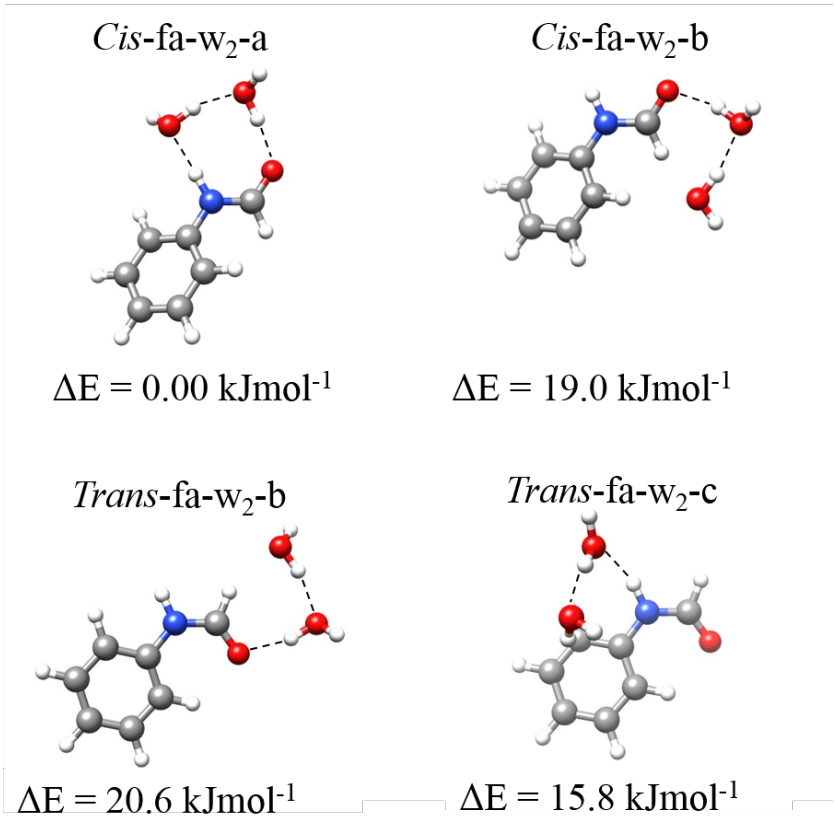


Figure S3. Predicted *cis*-fa-w-a and *cis*-fa-w-a' forms showing different arrangement of the water molecule with respect to *cis*-formanilide

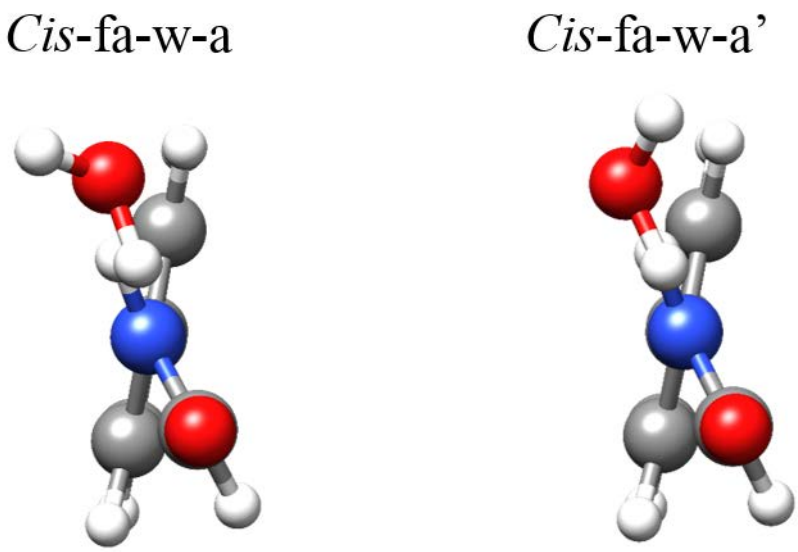


Figure S4. Predicted *cis*-fa-w_2-a and *cis*-fa-w_2-a' forms showing different arrangement of the water molecules with respect to *cis*-formanilide.

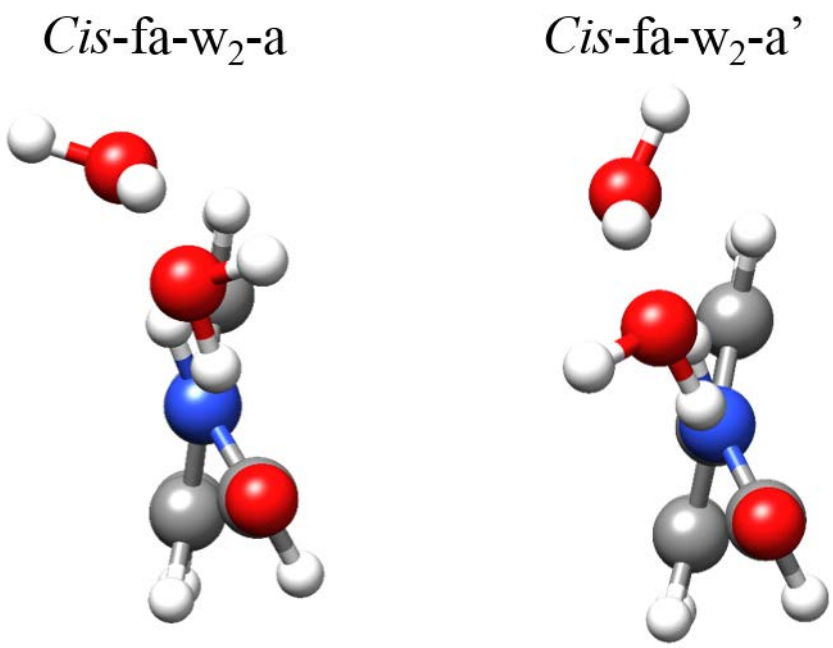


Figure S5. (a) Possible interconversion paths between *cis*-fa-w-a and *cis*-fa-w-a' forms. (b) The interconversion between the two equivalent *cis*-fa-w-a forms is a concerted $\angle C_1$-N-C_2-C_3 torsion + H_2O flipping motion. Any of $\angle C_1$-N-C_2-C_3 torsion or H_2O flipping motions provide a path for collisional relaxation in the supersonic jet from the higher energy *cis*-fa-w-a' form to the global minimum conformation *cis*-fa-w-a.

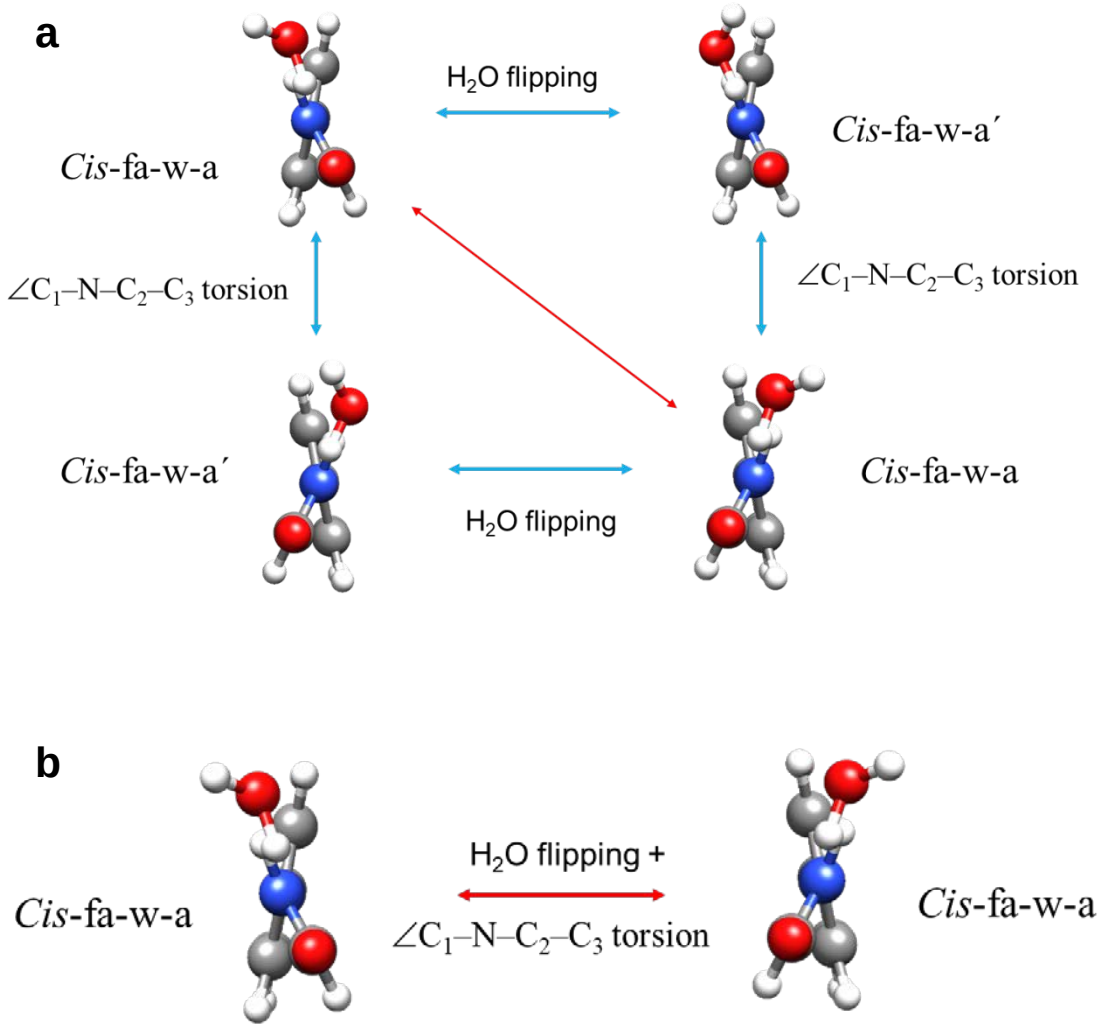


Figure S6. Correlation between the predicted χ_{zz} constant values for *cis*-fa [ref. 22], the mono and the dihydrated complexes and those for the r_e(C-N) (left axis, red dots) and r_e(C=O) (right axis, blue triangles) distances. All the distances are in Å.

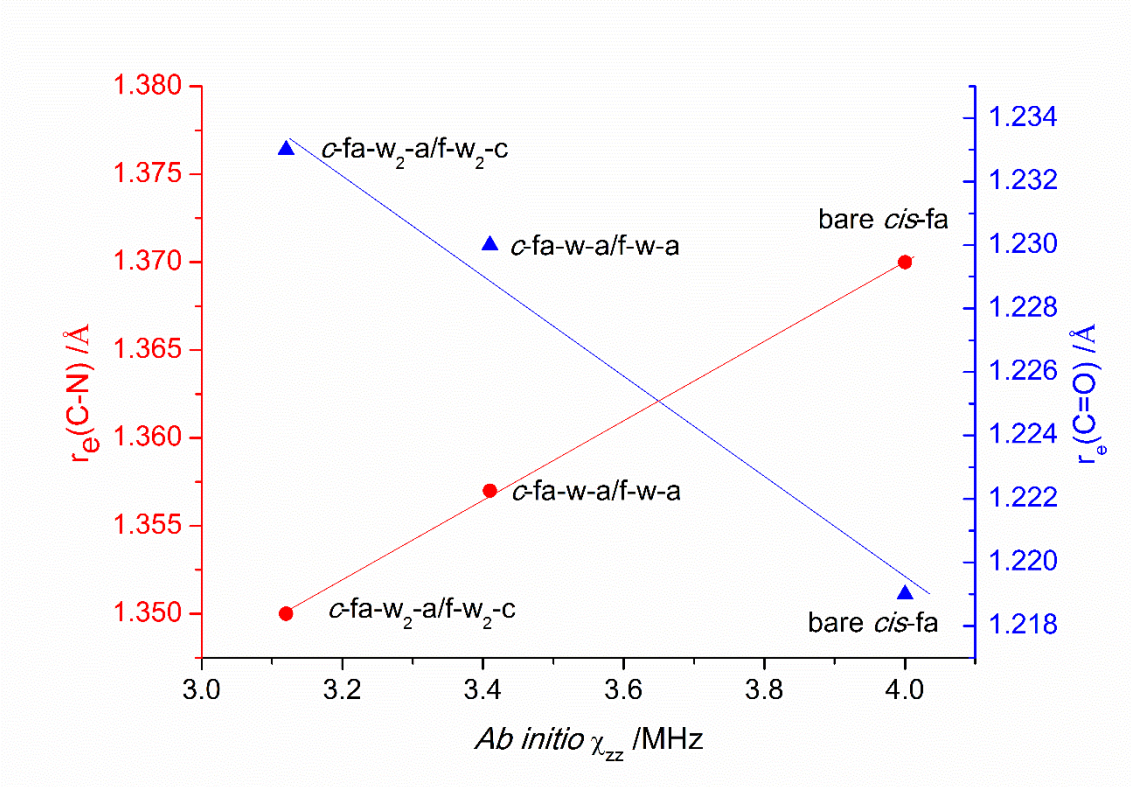


Table S1. *Ab initio* rotational parameters calculated at B3LYP-D3/6-311++G(d,p) level of theory for the *cis*-formanilide (*cis*-fa) and *trans*-formanilide (*trans*-fa) complexes with one molecule of water.

Parameter[a]	*Cis*-fa-w-a	*Cis*-fa-w-a'	*Cis*-fa-w-b	*Trans*-fa-w-a	*Trans*-fa-w-b	*Trans*-fa-w-c
A /MHz	2831.32	2839.04	3036.62	1870.86	4122.42	1562.54
B /MHz	663.09	660.98	555.65	866.31	538.12	948.66
C /MHz	550.06	549.98	479.17	593.41	476.03	591.93
P_a /uÅ^2	751.21	752.74	898.90	582.45	939.11	531.53
P_b /uÅ^2	167.56	166.16	155.80	269.21	122.55	322.24
P_c /uÅ^2	10.94	11.85	10.63	0.92	0.05	1.19
Δ_J /kHz	0.038	0.039	0.128	0.160	0.025	0.311
Δ_{JK} /kHz	-0.024	-0.002	-1.602	-0.216	0.483	-1.462
Δ_K /kHz	1.759	1.717	11.108	1.168	2.229	2.901
δ_J /kHz	0.009	0.009	0.028	0.059	0.003	0.141
δ_K /kHz	0.384	0.445	0.656	0.341	0.272	0.078
μ_a /D	2.35	-2.34	-3.36	-2.02	-2.77	2.55
μ_b /D	0.30	0.76	1.01	3.77	1.47	5.80
μ_c /D	-1.11	-0.93	-0.42	0.84	0.39	0.00
^{14}N χ_{aa} /MHz	2.29	2.28	2.14	1.84	1.98	2.18
^{14}N χ_{bb} /MHz	0.93	1.01	1.53	1.99	1.90	1.36
^{14}N χ_{cc} /MHz	-3.21	-3.30	-3.67	-3.82	-3.88	-3.54
ΔE /cm^{-1}	0.0	35.5	1335.8	1299.5	1088.2	983.0
ΔE /kJmol^{-1}	0.0	0.4	16.0	15.5	13.0	11.8
D_e /kJmol^{-1}	46.4	46.4	31.4	27.5	30.3	28.8

[a] *A*, *B* and *C* are the rotational constants. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. μ_α (α = *a*, *b* or *c*) are the electric dipole moment components, 1 D = $3.33\cdot10^{-30}$ C·m. χ_{aa}, χ_{bb}, and χ_{cc}, are the quadrupole coupling tensor diagonal elements for ^{14}N atom. ΔE is the energy relative to the most stable conformer. D_e is the dissociation energy calculated using the counterpoise procedure.

Table S2. *Ab initio* rotational parameters calculated at MP2/6-311++G(2d,p) level of theory for the *cis*-formanilide (*cis*-fa) and *trans*-formanilide (*trans*-fa) complexes with one molecule of water.

Parameter[a]	*Cis*-fa-w-a	*Cis*-fa-w-a'	*Cis*-fa-w-b	*Trans*-fa-w-a	*Trans*-fa-w-b	*Trans*-fa-w-c
A /MHz	2840.71	2851.89	2910.66	1830.28	4125.16	1561.92
B /MHz	664.06	659.95	569.75	889.16	542.43	942.17
C /MHz	554.39	554.93	490.67	602.60	479.62	589.30
P_a /uÅ^2	747.36	749.65	871.68	565.46	931.44	535.22
P_b /uÅ^2	164.23	161.07	158.30	273.20	122.25	322.38
P_c /uÅ^2	13.68	16.14	15.33	2.92	0.26	1.18
Δ_J /kHz	0.038	0.038	0.127	2.231	0.026	0.318
Δ_{JK} /kHz	0.015	0.074	-1.216	-5.732	0.315	3.035
Δ_K /kHz	1.779	1.674	8.640	7.285	1.751	-1.521
δ_J /kHz	0.009	0.007	0.027	0.576	0.003	0.143
δ_K /kHz	0.430	0.531	0.785	1.940	0.228	0.068
μ_a /D	2.26	2.26	3.23	1.51	2.57	-2.74
μ_b /D	0.34	0.86	1.06	3.72	1.55	5.47
μ_c /D	-1.11	0.85	0.46	-0.97	-0.66	0.00
^{14}N χ_{aa} /MHz	2.24	2.23	2.06	1.68	1.90	2.10
^{14}N χ_{bb} /MHz	0.66	0.77	1.34	1.84	1.71	1.21
^{14}N χ_{cc} /MHz	-2.89	-3.00	-3.40	-3.52	-3.60	-3.31
ΔE /cm^{-1}	0.0	38.3	1254.1	1293.3	1038.2	850.4
ΔE /kJmol^{-1}	0.0	0.5	15.0	15.5	12.4	10.2
D_e /kJmol^{-1}	38.6	38.6	25.7	23.1	25.1	24.6

[a] *A*, *B* and *C* are the rotational constants. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. μ_α (α = *a*, *b* or *c*) are the electric dipole moment components, 1 D = $3.33\cdot10^{-30}$ C·m. χ_{aa}, χ_{bb}, and χ_{cc}, are the quadrupole coupling tensor diagonal elements for ^{14}N atom. ΔE is the energy relative to the most stable conformer. D_e is the dissociation energy calculated using the counterpoise procedure.

Table S3. *Ab initio* rotational parameters calculated at B3LYP-D3/6-311++G(d,p) level of theory for the *cis*-formanilide (*cis*-fa) and *trans*-formanilide (*trans*-fa) complexes with two molecule of water.

Parameter[a]	*Cis*-fa-w_2-a	*Cis*-fa-w_2-a'	*Cis*-fa-w_2-b	*Trans*-fa-w_2-b	*Trans*-fa-w_2-c
A /MHz	2016.92	2040.30	1926.49	2645.14	1012.56
B /MHz	496.28	487.95	486.09	385.61	876.91
C /MHz	406.85	403.62	389.87	336.95	554.24
P_a /uÅ^2	1004.96	1020.06	1036.81	1309.69	494.52
P_b /uÅ^2	237.20	232.04	259.47	190.17	417.32
P_c /uÅ^2	13.37	15.66	2.86	0.89	81.79
Δ_J /kHz	0.049	0.045	0.048	0.011	0.602
Δ_{JK} /kHz	-0.384	-0.375	-0.285	0.091	-1.347
Δ_K /kHz	2.134	2.373	2.232	0.596	0.855
δ_J /kHz	0.015	0.011	0.013	0.001	0.096
δ_K /kHz	0.207	0.253	0.121	0.077	-1.495
μ_a /D	-1.84	-1.98	-1.95	-1.98	0.00
μ_b /D	0.61	0.47	0.00	-1.43	-3.78
μ_c /D	-0.01	0.21	0.37	-0.22	-0.57
^{14}N χ_{aa} /MHz	2.12	2.13	1.86	1.99	2.20
^{14}N χ_{bb} /MHz	0.97	1.03	1.37	1.81	0.75
^{14}N χ_{cc} /MHz	-3.09	-3.16	-3.23	-3.80	-2.95
ΔE /cm^{-1}	0.0	197.3	1634.4	1744.7	1711.6
ΔE /kJmol^{-1}	0.0	2.4	19.6	20.9	20.5
D_e /kJmol^{-1}	99.6	99.6	82.2	77.3	75.7

[a] *A*, *B* and *C* are the rotational constants. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. μ_α (α = *a*, *b* or *c*) are the electric dipole moment components, 1 D = $3.33\cdot10^{-30}$ C·m. χ_{aa}, χ_{bb}, and χ_{cc}, are the quadrupole coupling tensor diagonal elements for ^{14}N atom. ΔE is the energy relative to the most stable conformer. D_e is the dissociation energy calculated using the counterpoise procedure.

Table S4. *Ab initio* rotational parameters calculated at MP2/6-311++G(2d,p) level of theory for the *cis*-formanilide (*cis*-fa) and *trans*-formanilide (*trans*-fa) complexes with two molecule of water.

Parameter[a]	*Cis*-fa-w_2-a	*Cis*-fa-w_2-a'	*Cis*-fa-w_2-b	*Trans*-fa-w_2-b	*Trans*-fa-w_2-c
A /MHz	2007.09	2029.38	1885.33	2625.78	1019.09
B /MHz	496.02	486.15	490.98	386.22	894.62
C /MHz	408.56	406.36	391.60	337.32	571.63
P_a /uÅ^2	1002.02	1017.10	1025.91	1307.15	476.55
P_b /uÅ^2	234.94	226.58	264.63	191.08	407.56
P_c /uÅ^2	16.85	22.46	3.43	1.39	88.36
Δ_J /kHz	0.051	0.051	0.056	0.013	0.428
Δ_{JK} /kHz	-0.372	-0.389	2.410	0.114	0.364
Δ_K /kHz	2.175	2.576	-0.315	0.722	-0.640
δ_J /kHz	0.015	0.011	0.015	0.002	0.086
δ_K /kHz	0.221	0.282	0.134	0.103	2.337
μ_a /D	-1.76	-1.92	-1.85	-1.83	-1.06
μ_b /D	0.69	0.58	-0.03	1.38	3.38
μ_c /D	-0.01	0.28	-0.39	0.18	0.75
^{14}N χ_{aa} /MHz	2.07	2.09	1.78	1.92	2.31
^{14}N χ_{bb} /MHz	0.79	0.86	1.30	1.61	0.66
^{14}N χ_{cc} /MHz	-2.86	-2.95	-3.08	-3.53	-2.96
ΔE /cm^{-1}	0.0	197.5	1587.3	1719.3	1320.2
ΔE /kJmol^{-1}	0.0	2.4	19.0	20.6	15.8
D_e /kJmol^{-1}	81.3	81.3	66.6	61.9	62.9

[a] *A*, *B* and *C* are the rotational constants. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. μ_α (α = *a*, *b* or *c*) are the electric dipole moment components, 1 D = $3.33\cdot10^{-30}$ C·m. χ_{aa}, χ_{bb}, and χ_{cc}, are the quadrupole coupling tensor diagonal elements for ^{14}N atom. ΔE is the energy relative to the most stable conformer. D_e is the dissociation energy calculated using the counterpoise procedure.

Table S5. Observed rotational parameters obtained for the *cis*-fa-w-a complex for the parent species, $^{2}H_{w1}$, $^{2}H_{w2}$, $^{2}H_{1}$ and the $^{18}O_{w}$ observed isotopologues compared to the *ab initio* (MP2/6-311++G(2d,p)) values. (See figure 1 for notation).

Fitted Parameters[a]	Parent		$^{18}O_w$		*ab initio*	*ab initio* (33.6°)[d]
	v=0	v=1	v=0	v=1		
A /MHz	2831.4048(56)[b]		2759.106(12)		2841	2834
B /MHz	662.38699(14)	662.38850(14)	643.35029(13)	643.34919(13)	664	666
C /MHz	549.51811(11)		533.950622(85)		554	552
Δ_J /kHz	0.04469(47)		[0.04469][c]		0.038	
δ_J /kHz	0.01078(36)		[0.01078]		0.009	
δ_K /kHz	0.480(27)		[0.480]		0.430	
^{14}N 3/2(χ_{aa}) /MHz	3.2149(93)		[3.2149]		3.36	
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	0.9885(67)		[0.9885]		0.89	
n	246/41/41		89/15/15			
σ /kHz	2.5/2.9/2.0		3.8/3.8/3.8			
Derived Parameters						
P_a /uÅ^2	752.07627(21)		774.09936(42)		747.4	747.8
P_b /uÅ^2	167.60044(21)		172.39079(42)		164.2	167.2
P_c /uÅ^2	10.89011(21)		11.44316(42)		13.7	10.9
^{14}N χ_{aa} /MHz	2.1433(61)		[2.1433]		2.24	
^{14}N χ_{bb} /MHz	0.905(16)		[0.905]		0.66	
^{14}N χ_{cc} /MHz	-3.049(16)		[-3.049]		-2.89	

[a] *A*, *B* and *C* are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. *n* is the number of total quadrupole hyperfine components fitted / rotational transitions fitted for the *v* = 0 state / rotational transitions fitted for the *v* = 1 state. σ is the total rms deviation of the fit / rms for the fit of the *v* = 0 state / rms for the fit of the *v* = 1 state. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digit. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit. [d] Rotational constants obtained by setting the C_1–N–C_2–C_3 dihedral angle to reproduce the experimental constants keeping fixed the rest of the molecular parameters.

Table S5. Continued.

Fitted Parameters[a]	Parent		$^2H_{w1}$	$^2H_{w2}$	$^2H_1$	*ab initio*	*ab initio* (33.6°)[d]
	v=0	v=1					
A /MHz	2831.4048(56)[b]		2829.08(10)	2766.81(10)	2817.460(78)	2841	2834
B /MHz	662.38699(14)	662.38850(14)	651.19251(60)	648.27840(81)	661.20570(57)	659	666
C /MHz	549.51811(11)		541.78375(55)	537.81920(76)	547.90770(59)	554	552
Δ_J /kHz	0.04469(47)		[0.04469][c]	[0.04469]	[0.04469]	0.038	
δ_J /kHz	0.01078(36)		[0.01078]	[0.01078]	[0.01078]	0.009	
δ_K /kHz	0.480(27)		[0.480]	[0.480]	[0.480]	0.430	
^{14}N 3/2(χ_{aa}) /MHz	3.2149(93)		[3.2149]	[3.2149]	[3.2149]	3.36	
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	0.9885(67)		[0.9885]	[0.9885]	[0.9885]	0.89	
n	246/41/41		29/18	27/12	28/13		
σ /kHz	2.5/2.9/2.0		7.6	9.5	6.1		
Derived Parameters							
P_a /uÅ^2	752.07627(21)		765.1254(64)	768.2976(68)	753.6677(26)	747.4	747.8
P_b /uÅ^2	167.60044(21)		167.6803(64)	171.3843(68)	168.7122(26)	164.2	167.2
P_c /uÅ^2	10.89011(21)		10.9569(64)	11.2733(68)	10.6618(26)	13.7	10.9
^{14}N χ_{aa} /MHz	2.1433(61)		[2.1433]	[2.1433]	[2.1433]	2.24	
^{14}N χ_{bb} /MHz	0.905(16)		[0.905]	[0.905]	[0.905]	0.66	
^{14}N χ_{cc} /MHz	-3.049(16)		[-3.049]	[-3.049]	[-3.049]	-2.89	

[a] *A*, *B* and *C* are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. *n* is the number of total quadrupole hyperfine components fitted / rotational transitions fitted for the *v* = 0 state / rotational transitions fitted for the *v* = 1 state. σ is the total rms deviation of the fit / rms for the fit of the *v* = 0 state / rms for the fit of the *v* = 1 state. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digit. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit. [d] Rotational constants obtained by setting the C_1–N–C_2–C_3 dihedral angle to reproduce the experimental constants keeping fixed the rest of the molecular parameters.

Table S6. Observed rotational parameters obtained for the *trans*-fa-w-b complex for the parent species and the observed isotopologues compared to the *ab initio* (MP2/6-311++G(2d,p)) values. (See figure 1 for notation).

Fitted Parameters[a]	Parent	$^{18}O_w$	$^{2}H_{w1}$	*ab initio*	*ab initio* planar[d]
A /MHz	4094.8678(75)[b]	4093.4250(30)	4078.59(36)	4125	4015
B /MHz	539.02116(10)	513.41306(10)	530.25227(59)	542	545
C /MHz	476.89366(10)	456.722450(81)	469.82724(55)	480	481
Δ_J /kHz	0.02959(23)	[0.02959][c]	[0.02959]	0.026	
Δ_{JK} /kHz	0.4586(77)	[0.4586]	[0.4586]	0.315	
Δ_K /kHz	4.44(74)	[4.44]	[4.44]	1.751	
δ_J /kHz	0.00323(27)	[0.00323]	[0.00323]	0.003	
^{14}N 3/2(χ_{aa}) /MHz	2.802(16)	[2.802]	[2.802]	2.85	
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.3153(44)	[1.3153]	[1.3153]	1.33	
n	111/38	33/11	18/11		
σ /kHz	2.5	2.3	7.3		
Derived Parameters					
P_a /uÅ^2	936.94997(36)	983.71235(29)	952.425(11)	931.4	926.5
P_b /uÅ^2	122.78105(36)	122.82184(29)	123.244(11)	122.2	125.1
P_c /uÅ^2	0.63661(36)	0.63932(29)	0.666(11)	0.3	0.8
^{14}N χ_{aa} /MHz	1.868(11)	[1.868]	[1.868]	1.90	
^{14}N χ_{bb} /MHz	1.697(14)	[1.697]	[1.697]	1.71	
^{14}N χ_{cc} /MHz	-3.565(14)	[-3.565]	[-3.565]	-3.60	

[a] *A*, *B* and *C* are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. *n* is the number of total quadrupole hyperfine components fitted / rotational transitions fitted. σ is the rms deviations of the fit. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digit. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit. [d] Rotational constants obtained by constraining the structure in a plane with the exception of the H_{w2} atom.

Table S7. Observed rotational parameters obtained for the *trans*-fa-w-c complex for the parent species and the $^{18}O_w$ observed isotopologue compared to the *ab initio* (MP2/6-311++G(2d,p)) values. (See figure 1 for notation).

Fitted Parameters[a]	Parent		$^{18}O_w$		*ab initio*
	v=0	v=1	v=0	v=1	
A /MHz	1608.09000(26)[b]	1607.55924(26)	1562.3190(27)	1561.7594(27)	1562
B /MHz	907.81842(11)	907.76796(11)	878.7953(10)	878.7719(10)	942
C /MHz	581.604742(46)	581.640188(46)	563.67834(14)	563.71477(14)	589
Δ_J /kHz	0.4732(12)		[0.4732][c]		0.318
Δ_{JK} /kHz	5.711(18)		[5.711]		3.035
Δ_K /kHz	-2.6208(51)		[-2.6208]		-1.521
δ_J /kHz	0.21434(63)		[0.21434]		0.143
δ_K /kHz	0.1124(65)		[0.1124]		0.068
^{14}N 3/2(χ_{aa}) /MHz	3.0600(42)		[3.0600]		3.24
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	1.16089(85)		[1.16089]		1.19
n	274/46/46		48/6/6		
σ /kHz	1.3/1.3/1.3		1.1/1.0/1.2		
Derived Parameters					
P_a /uÅ^2	555.68112(11)	555.61823(11)	574.08748(89)	574.00822(89)	535.2
P_b /uÅ^2	313.25781(11)	313.26775(11)	322.48592(89)	322.50724(89)	322.4
P_c /uÅ^2	1.01502(11)	1.10885(11)	0.99411(89)	1.08870(89)	1.2
^{14}N χ_{aa} /MHz	2.0400(28)		[2.0400]		2.10
^{14}N χ_{bb} /MHz	1.3018(31)		[1.3018]		1.21
^{14}N χ_{cc} /MHz	-3.3418(31)		[-3.3418]		-3.31

[a] *A*, *B* and *C* are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. *n* is the number of total quadrupole hyperfine components fitted / rotational transitions fitted for the *v* = 0 state / rotational transitions fitted for the *v* = 1 state. σ is the total rms deviation of the fit / rms for the fit of the *v* = 0 state / rms for the fit of the *v* = 1 state. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digit. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit.

Table S8. Observed rotational parameters obtained for the *cis*-fa-w_2-a complex for the parent species and the $^{18}O_w$ observed isotopologues compared to the *ab initio* (MP2/6-311++G(2d,p)) values. (See figure 1 for notation).

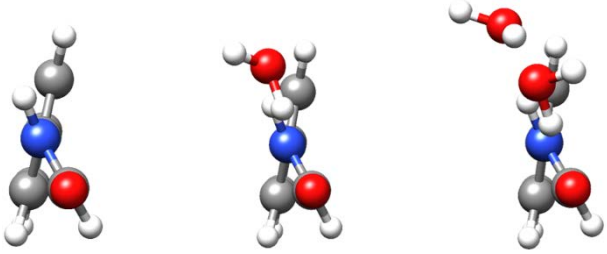
Fitted Parameters[a]	Parent	$^{18}O_{w1}$	$^{18}O_{w2}$	*ab initio*	*ab initio* (33.3°)[d]
A /MHz	1992.9001(14)[b]	1928.1500(92)	1991.1356(48)	2007	2005
B /MHz	494.434394(34)	489.95744(10)	477.788224(49)	496	497
C /MHz	405.007349(26)	399.433590(87)	393.704503(37)	408	407
Δ_J /kHz	0.058560(87)	[0.058560][c]	[0.058560]	0.051	
Δ_{JK} /kHz	-0.4858(11)	[-0.4858]	[-0.4858]	-0.372	
δ_J /kHz	0.016610(57)	[0.016610]	[0.016610]	0.015	
δ_K /kHz	0.1667(46)	[0.1667]	[0.1667]	0.221	
^{14}N 3/2(χ_{aa}) /MHz	3.0130(72)	[3.0130]	[3.0130]	3.10	
^{14}N ¼(χ_{bb}-χ_{cc}) /MHz	0.9797(23)	[0.9797]	[0.9797]	0.91	
n	156/52	33/11	36/12		
σ /kHz	0.8	2.6	1.4		
Derived Parameters					
P_a /uÅ^2	1008.18632(21)	1017.3043(13)	1043.79149(63)	1002.0	1002.0
P_b /uÅ^2	239.64043(21)	247.9347(13)	239.85907(63)	234.9	238.1
P_c /uÅ^2	13.94930(21)	14.1709(13)	13.95539(63)	16.8	14.0
^{14}N χ_{aa} /MHz	2.0087(48)	[2.0087]	[2.0087]	2.07	
^{14}N χ_{bb} /MHz	0.9551(70)	[0.9551]	[0.9551]	0.79	
^{14}N χ_{cc} /MHz	-2.9637(70)	[-2.9637]	[-2.9637]	-2.86	

[a] *A*, *B* and *C* are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. χ_{aa}, χ_{bb} and χ_{cc} are the quadrupole coupling tensor diagonal elements for ^{14}N atom. *n* is the number of total quadrupole hyperfine components fitted / rotational transitions fitted. σ is the rms deviations of the fit. P_α (α= *a*, *b* or *c*) are the planar moments of inertia, these are derived from the moments of inertia I_α as for example $P_c = (I_a+I_b-I_c)/2$. [b] Standard errors are given in parentheses in units of the last digit. [c] Parameters in square brackets were kept fixed to those given for the parent species in the fit. [d] Rotational constants obtained by setting the C_1–N–C_2–C_3 dihedral angle to reproduce the experimental constants keeping fixed the rest of the molecular parameters.

Table S9. Comparison of the planar moments of inertia for the observed complexes in this work with the values reported [ref. 22] for the monomers of *cis* and *trans* formanilide.

	Cis-fa	*Cis*-fa-w-a	*Cis*-fa-w_2-a
P_a /uÅ^2	539.9978(10)	752.07627(21)	1008.18632(21)
P_b /uÅ^2	95.9417(10)	167.60044(21)	239.64043(21)
P_c /uÅ^2	3.9009(10)	10.89011(21)	13.94930(21)

Cis-fa *Cis*-fa-w-a *Cis*-fa-w_2-a



	Trans-fa	*Trans*-fa-w-b	*Trans*-fa-w-c
P_a /uÅ^2	449.44891(15)	936.94997(36)	555.68112(11)
P_b /uÅ^2	119.61512(15)	122.78105(36)	313.25781(11)
P_c /uÅ^2	0.30034(15)	0.63661(36)	1.01502(11)

Trans-fa *Trans*-fa-w-b *Trans*-fa-w-c

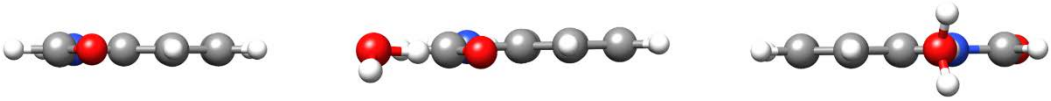


Table S10. r_s structure for the *cis*-fa-w-a complex and its comparison with r_e (MP2/6-311++G(2d,p)) structure and the r_0 structure obtained from the fit of the rotational constants for all the available isotopologues. In the fit, the geometrical parameters for water were fixed to its r_0 values [Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J., Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619–721]. The hydrogen bond structure is compared to that of the related formamide-w-a complex (ref. [16]).

	atom	*a*	*b*	*c*
$\lvert r_s \rvert$		|3.35040(45)|	|1.52958(99)|	|0.3436(44)|
r_0	O_w	-3.3519(9)	-1.54(1)	0.323(2)
r_e		-3.331	-1.526	0.363
$\lvert r_s \rvert$		|3.61365(61)|	|0.2860(78)|	|0.2613(85)|
r_0	H_{w1}	-3.5768(5)	-0.607(1)	0.147(1)
r_e		-3.560	-0.601	0.148
$\lvert r_s \rvert$		|4.01537(56)|	|1.9705(12)|	|0.6337(37)|
r_0	H_{w2}	-3.970(1)	-1.850(2)	0.998(3)
r_e		-3.957	-1.809	1.036
$\lvert r_s \rvert$		|1.26(1)|	|1.06(1)|	|0.48i|
r_0	H_1	-1.4868(3)	-0.795(1)	0.262(1)
r_e		-1.496	-0.786	0.323

$\lvert r_s \rvert$		1.2737(77)
r_0	$r(O_w\text{-}H_{w1})$	0.979(2)
r_e		0.971
$\lvert r_s \rvert$		0.8490(22)
r_0	$r(O_w\text{-}H_{w2})$	0.965(3)
r_e		0.959
$\lvert r_s \rvert$		-
r_0	$r(O_w\cdots H_1)$	2.011(1)
r_e		1.976

Fitted parameter	r_0	r_e	f-w-a[a]
$r(H_{w1}\cdots O_1)$ /Å	1.931(3)	1.925	1.93(1)
$\angle(H_{w1}\cdots O_1\text{–}C_1)$ /°	108.24(4)	107.4	110.3(3)
$\angle(C_1\text{–}N\text{–}C_2\text{–}C_3)$ /°	33.5(1)	[33.6]	

Derived parameter	r_0	r_e	f-w-a
$r(O_w\cdots H_1)$ /Å	2.011(1)	1.976	2.061(4)
$r(O_w\cdots O_1)$ /Å	2.804(2)	2.796	
$r(O_w\cdots N)$ /Å	2.890(1)	2.858	
$\angle(N\text{–}H_1\cdots O_w)$ /°	142.56(8)	142.8	139.5(3)
$\angle(H_1\cdots O_w\text{–}H_{w1})$ /°	81.46(8)	81.9	78.2(6)
$\angle(N\cdots O_w\cdots O_1)$ /°	47.39(2)	47.75	
$\angle(O_w\cdots O_1\cdots N)$ /°	68.27(3)	67.55	
$\angle(O_1\cdots N\cdots O_w)$ /°	64.35	64.69	
$\angle(H_{w2}\text{–}O_w\cdots O_1\cdots N)$ /°	130.7(2)	130.4	

Fixed parameter	r_0	r_e	f-w-a
$\angle(O_w\text{–}H_{w1}\cdots O_1)$ /°	[147.20(7)]	147.2	153(1)

[a] r_0 structure for formamide-w-a, [ref. 16]

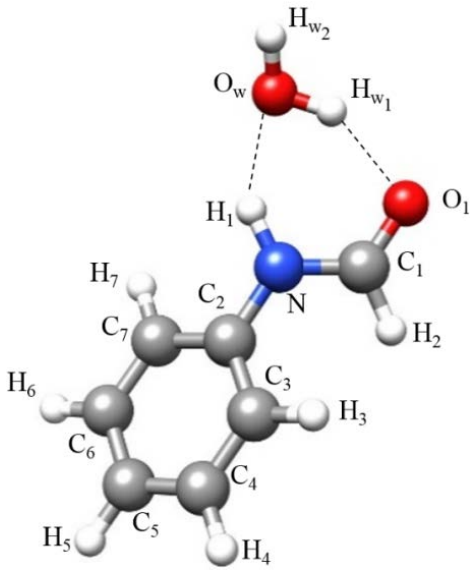


Table S11. r_s structure for the *cis*-fa-w_2-a complex and its comparison with r_e (MP2/6-311++G(2d,p)) structure and the r_0 structure obtained from the fit of the rotational constants for all the available isotopologues. In the fit, the geometrical parameters for water were fixed to its r_0 values [Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J., Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619–721]. The hydrogen bond structure is compared to that of the related formamide-w_2-a complex (ref. [16]).

	atom	*a*	*b*	*c*
$\lvert r_s \rvert$		|4.24103(35)|	|0.3399(44)|	|0.056(27)|
r_0	O_{w1}	-4.244(1)	-0.356(6)	0.007(2)
r_e		-4.224	0.357	-0.026
$\lvert r_s \rvert$		|2.13464(71)|	|2.05833(73)|	|0.3422(44)|
r_0	O_{w2}	-2.140(3)	-2.060(4)	0.353(1)
r_e		-2.121	2.047	-0.376

$\lvert r_s \rvert$		2.7327(39)
r_0	$r(O_{w1}\text{-}O_{w2})$	2.727(5)
r_e		2.721

Fitted parameter	r_0	r_e	f-w_2-a[a]
$r(O_1\cdots H_{w1})$ /Å	1.809(7)	1.788	1.797(8)
$r(H_1\cdots O_{w2})$ /Å	1.874(4)	1.845	1.874(4)
$\angle(H_{w1}\cdots O_1\text{–}C_1)$ /°	128.1(3)	127.8	130.2(8)
$\angle(O_{w2}\cdots H_1\text{–}N)$ /°	176.5(2)	175.4	178.9(3)
$\angle(C_1\text{–}N\text{–}C_2\text{–}C_3)$ /°	32.73(9)	[33.3]	

Derived parameter	r_0	r_e	f-w_2-a
$r(O_{w1}\cdots H_{w3})$ /Å	1.777(6)	1.775	1.829(4)
$r(O_{w1}\cdots O_1)$ /Å	2.784(5)	2.761	2.784(5)
$r(O_{w2}\cdots N)$ /Å	2.902(4)	2.872	2.902(4)
$r(O_{w1}\cdots O_{w2})$ /Å	2.727(5)	2.721	2.727(5)
$\angle(H_1\cdots O_{w2}\text{–}H_{w3})$ /°	96.2(4)	96.4	97.6(7)
$\angle(O_{w2}\text{–}H_{w3}\cdots O_{w1})$ /°	161.0(5)	160.4	160(1)
$\angle(H_{w3}\cdots O_{w1}\text{–}H_{w1})$ /°	99.9(2)	100.1	99(1)
$\angle(N\cdots O_{w2}\cdots O_{w1})$ /°	84.5(1)	84.4	
$\angle(O_{w2}\cdots O_{w1}\cdots C_1)$ /°	86.7(1)	86.9	
$\angle(O_{w1}\cdots C_1\text{–}N)$ /°	96.0(1)	95.7	
$\angle(C_1\text{–}N\cdots O_{w2})$ /°	92.8(1)	93.0	
$\angle(H_{w2}\text{–}O_{w1}\cdots O_1\cdots N)$ /°	-130.7(3)	-130.7	
$\angle(H_{w4}\text{–}O_{w2}\cdots O_1\cdots N)$ /°	96.8(4)	97.0	

Fixed parameter	r_0	r_e	f-w_2
$\angle(O_{w1}\text{–}H_{w1}\cdots O_1)$ /°	[169.9(3)]	169.9	171(2)

[a] r_0 structure for formamide-w_2-a, [ref. 16]

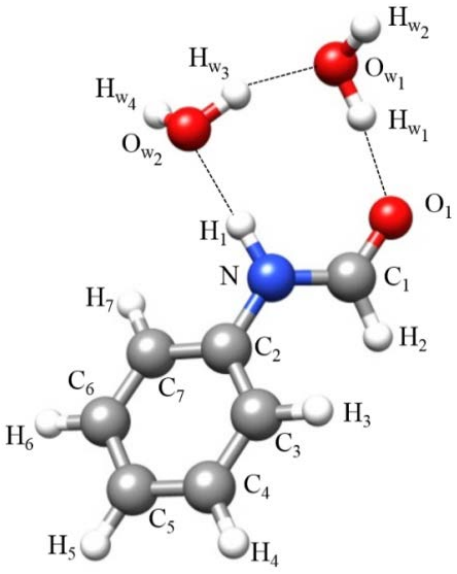


Table S12. r_s structure for the *trans*-fa-w-b complex and its comparison with r_e (MP2/6-311++G(2d,p)) structure and the r_0 structure obtained from the fit of the rotational constants for all the available isotopologues. In the fit, the geometrical parameters for water were fixed to its r_0 values [Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J., Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619–721]. The hydrogen bond structure is compared to that of the related formamide-w-b complex (ref. [16]).

	atom	*a*	*b*	*c*
$\lvert r_s \rvert$		|4.86484(31)|	|0.147(10)|	|0.038(39)|
r_0	O_w	-4.8670(9)	0.164(8)	-0.0513(4)
r_e		-4.837	-0.132	0.053
$\lvert r_s \rvert$		|3.93463(80)|	|0.6872(46)|	|0.172(18)|
r_0	H_{w1}	-3.998	-0.622	0.0067(3)
r_e		3.978	-0.620	-0.006

$\lvert r_s \rvert$		1.0837(78)
r_0	$r(O_w\text{-}H_{w1})$	0.975(5)
r_e		0.969

Fitted parameter	r_0	r_s	r_e	f-w-b[a]
$r(H_{w1}\cdots O_1)$ /Å	1.941(3)	1.0837(78)	1.929	1.932
$\angle(H_{w1}\cdots O_1\text{–}C_1)$ /°	100.8(3)		98.8	110.3(3)

Derived parameter	r_0	r_e	f-w-b
$r(O_w\cdots H_2)$ /Å	2.681(7)	2.603	2.715
$r(O_w\cdots O_1)$ /Å	2.841(3)	2.827	
$\angle(C\text{–}H_2\cdots O_w)$ /°	103.5(6)	104.8	104.0
$\angle(H_2\cdots O_w\text{–}H_{w1})$ /°	61.6(4)	62.3	59.1
$\angle(H_{w2}\text{–}O_w\cdots O_1\cdots N)$ /°	151.0(5)	151.1	

Fixed parameter	r_0	r_e	f-w-b
$\angle(O_w\text{–}H_{w1}\cdots O_1)$ /°	[152.3(5)]	152.3	155.4

[a] r_0 structure for formamide-w-b, [ref. 16]

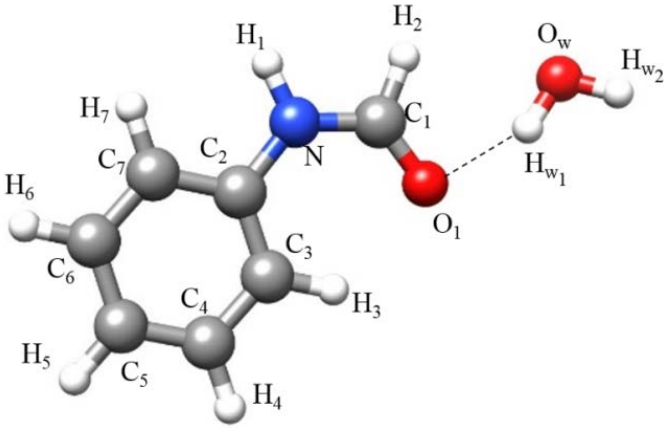


Table S13. r_s structure for the *trans*-fa-w-c complex and its comparison with r_e (MP2/6-311++G(2d,p)) structure and the r_0 structure obtained from the fit of the rotational constants for all the available isotopologues. In the fit, the geometrical parameters for water were fixed to its r_0 values [Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J., Maki, A. G. *J. Phys. Chem. Ref. Data* 1979, 8, 619–721]. The hydrogen bond structure is compared to that of the related formamide-w-c complex (ref. [16]).

	atom	*a*	*b*	*c*
$\lvert r_s \rvert$		|2.99363(50)|	|2.24178(67)|	|0.105i|
r_0	O_w	-3.0135(9)	-2.2249(6)	[0.000]
r_e		-2.788	-2.373	0.000

Fitted parameter	r_0	r_e	f-w-c[a]
$r(O_w\cdots H_1)$ /Å	2.0093(9)	1.992	2.008
$\angle(O_w\cdots H_1\text{–}N)$ /°	184.85(3)	177.2	177.6

Derived parameter	r_0	r_e	f-w-c
$r(O_w\cdots N)$ /Å	3.0236(8)	3.008	3.019

Fixed parameter	r_0	r_e	f-w-c
$\angle(H_1\cdots O_w\text{–}H_{w1})$ /°	[124.45(7)]	124.45	126.8
$\angle(H_1\cdots O_w\text{–}H_{w2})$ /°	[124.45(7)]	124.45	126.8
$\angle(N\text{–}H_1\cdots O_w\text{–}H_{w1})$ /°	[105.5(1)]	105.5	84.0
$\angle(N\text{–}H_1\cdots O_w\text{–}H_{w2})$ /°	[-105.5(1)]	-105.5	-84.0

[a] *ab initio* structure for formamide-w-c, [ref. 16]

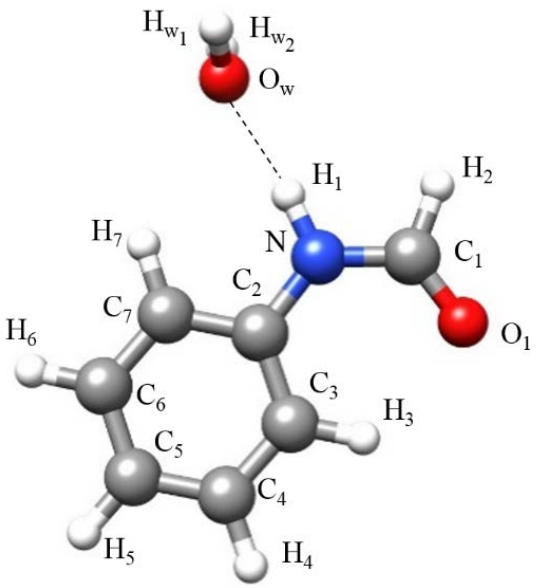


Table S14. Experimental and *ab initio* quadrupole coupling constants for *cis* and *trans*-formanilide [ref. 22] and their complexes, together with the predicted distances C_1=O_1 and C_1-N. (See figure 1 for notation).

Exp.	*Cis*-fa	*Cis*-fa-w-a	*Cis*-fa-w_2-a	*Trans*-fa	*Trans*-fa-w-b	*Trans*-fa-w-c
χ_{aa} /MHz	2.173(53)	2.1433(61)	2.0087(48)	1.9267(40)	1.868(11)	2.0400(28)
χ_{bb} /MHz	0.593(87)	0.905(16)	0.9551(70)	1.7447(60)	1.697(14)	1.3018(31)
χ_{cc} /MHz	-2.767(87)	-3.049(16)	-2.9637(70)	-3.6713(60)	-3.565(14)	-3.3418(31)
χ_{cc}/eQq_{210}	0.2767	0.3049	0.29637	0.36713	0.3565	0.33418
ab initio (MP2/6-311++G(2d,p))						
χ_{aa} /MHz	2.26	2.21	2.07	1.81	1.90	2.07
χ_{bb} /MHz	0.48	0.78	0.83	1.76	1.71	1.24
χ_{cc} /MHz	-2.74	-2.99	-2.90	-3.57	-3.60	-3.31
χ_{xx} /MHz	2.31	2.31	2.31	2.14	2.09	2.18
χ_{yy} /MHz	1.10	1.10	0.81	1.60	1.52	1.13
χ_{zz} /MHz	-4.00	-3.41	-3.12	-3.74	-3.61	-3.31
ab initio (MP2/6-311++G(2d,p))						
C_1=O_1 /Å	1.219	1.230	1.233	1.230	1.227	1.222
C_1-N /Å	1.370	1.357	1.350	1.376	1.361	1.365

Table S15. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the parent species of the complex *cis*-fa-w-a in the *v*=0 and *v*=1 vibrational states.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
5	1	5	4	1	4	*0*	*0*	6	5	5759.5790	0.0023
								4	3	5759.6336	0.0019
								5	4	5759.6540	0.0011
5	1	5	4	1	4	*1*	*1*	6	5	5759.5790	-0.0012
								4	3	5759.6336	-0.0016
								5	4	5759.6540	-0.0023
5	0	5	4	0	4	*0*	*0*	6	5	5975.4706	0.0031
								4	3	5975.4968	0.0014
								5	4	5975.5633	0.0023
5	0	5	4	0	4	*1*	*1*	6	5	5975.4706	-0.0015
								4	3	5975.4968	-0.0032
								5	4	5975.5648	-0.0007
5	2	4	4	2	3	*0*	*0*	4	3	6049.9068	0.0020
								6	5	6049.9233	0.0008
								5	4	6050.0894	0.0014
5	2	4	4	2	3	*1*	*1*	4	3	6049.9139	0.0016
								6	5	6049.9292	-0.0007
								5	4	6050.0952	-0.0002
5	3	3	4	3	2	*0*	*0*	4	3	6073.0434	-0.0002
								6	5	6073.1229	-0.0004
								5	4	6073.4409	0.0004
5	3	3	4	3	2	*1*	*1*	4	3	6073.0507	-0.0010
								6	5	6073.1314	0.0000
								5	4	6073.4489	0.0003
5	3	2	4	3	1	*0*	*0*	4	3	6075.1822	0.0001
								6	5	6075.2614	0.0003
								5	4	6075.5748	0.0008
5	3	2	4	3	1	*1*	*1*	4	3	6075.1927	0.0023
								6	5	6075.2692	0.0000
								5	4	6075.5824	0.0002
5	2	3	4	2	2	*0*	*0*	4	3	6133.9185	-0.0033
								6	5	6133.9303	-0.0004
								5	4	6134.0129	-0.0010
5	2	3	4	2	2	*1*	*1*	4	3	6133.9341	0.0022
								6	5	6133.9417	0.0009
								5	4	6134.0240	0.0000
5	1	4	4	1	3	*0*	*0*	4	3	6321.7700	-0.0004
								6	5	6321.7840	0.0000
								5	4	6321.8438	0.0000
5	1	4	4	1	3	*1*	*1*	4	3	6321.7792	-0.0020
								6	5	6321.7943	-0.0005
								5	4	6321.8550	0.0005
6	1	6	5	1	5	*0*	*0*	7	6	6901.2088	0.0007
								5	4	6901.2478	0.0009
								6	5	6901.2672	0.0003
6	1	6	5	1	5	*1*	*1*	7	6	6901.2124	0.0002
								5	4	6901.2511	0.0001

Table S15. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
6	1	6	5	1	5	*1*	*1*	6	5	6901.2709	0.0000
6	0	6	5	0	5	*0*	*0*	7	6	7127.5845	0.0021
								5	4	7127.6017	0.0026
								6	5	7127.6868	0.0026
6	0	6	5	0	5	*1*	*1*	7	6	7127.5845	-0.0031
								5	4	7127.6017	-0.0025
								6	5	7127.6868	-0.0025
6	2	5	5	2	4	*0*	*0*	7	6	7252.0734	-0.0007
								5	4	7252.0734	0.0011
								6	5	7252.1822	0.0009
6	2	5	5	2	4	*1*	*1*	7	6	7252.0819	-0.0010
								5	4	7252.0819	0.0008
								6	5	7252.1886	-0.0014
6	3	4	5	3	3	*0*	*0*	5	4	7292.1438	-0.0018
								7	6	7292.1753	0.0001
								6	5	7292.3581	0.0010
6	3	4	5	3	3	*1*	*1*	5	4	7292.1548	-0.0007
								7	6	7292.1863	0.0013
								6	5	7292.3671	0.0002
6	3	3	5	3	2	*0*	*0*	5	4	7297.8238	-0.0020
								7	6	7297.8545	0.0002
								6	5	7298.0290	0.0005
6	3	3	5	3	2	*1*	*1*	5	4	7297.8355	-0.0004
								7	6	7297.8655	0.0011
								6	5	7298.0386	0.0000
6	2	4	5	2	3	*0*	*0*	7	6	7395.8019	-0.0010
								5	4	7395.8070	-0.0018
								6	5	7395.8157	-0.0008
6	2	4	5	2	3	*1*	*1*	7	6	7395.8157	-0.0001
								5	4	7395.8227	0.0009
								6	5	7395.8326	0.0031
6	1	5	5	1	4	*0*	*0*	5	4	7572.7188	-0.0012
								7	6	7572.7268	-0.0007
								6	5	7572.7785	-0.0003
6	1	5	5	1	4	*1*	*1*	5	4	7572.7326	0.0007
								7	6	7572.7401	0.0007
								6	5	7572.7902	-0.0004
7	1	7	6	1	6	*0*	*0*	8	7	8038.0556	0.0008
								6	5	8038.0834	0.0000
								7	6	8038.1051	0.0004
7	1	7	6	1	6	*1*	*1*	8	7	8038.0594	0.0000
								6	5	8038.0882	0.0002
								7	6	8038.1093	0.0000
7	0	7	6	0	6	*0*	*0*	8	7	8260.9484	0.0010
								6	5	8260.9595	0.0010
								7	6	8261.0548	0.0014
7	0	7	6	0	6	*1*	*1*	8	7	8260.9510	-0.0018
								6	5	8260.9624	-0.0015
								7	6	8261.0572	-0.0015

Table S15. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
7	2	6	6	2	5	*0*	*0*	8	7	8449.9664	0.0011
								6	5	8449.9730	0.0017
								7	6	8450.0431	0.0014
7	2	6	6	2	5	*1*	*1*	8	7	8449.9730	-0.0021
								6	5	8449.9800	-0.0011
								7	6	8450.0499	-0.0016
7	4	4	6	4	3	*0*	*0*	6	5	8504.4505	0.0006
								8	7	8504.4831	0.0003
								7	6	8504.6870	-0.0002
7	4	4	6	4	3	*1*	*1*	6	5	8504.4613	0.0000
								8	7	8504.4928	-0.0013
								7	6	8504.7016	0.0029
7	4	3	6	4	2	*0*	*0*	6	5	8504.6990	0.0083
								8	7	8504.7239	0.0004
								7	6	8504.9284	0.0007
7	4	3	6	4	2	*1*	*1*	6	5	8504.7074	0.0053
								8	7	8504.7367	0.0018
								7	6	8504.9382	-0.0008
7	3	5	6	3	4	*0*	*0*	6	5	8512.7523	-0.0003
								8	7	8512.7655	0.0018
								7	6	8512.8778	0.0013
7	3	5	6	3	4	*1*	*1*	6	5	8512.7655	0.0013
								8	7	8512.7746	-0.0006
								7	6	8512.8877	-0.0003
7	3	4	6	3	3	*0*	*0*	6	5	8525.4546	-0.0001
								8	7	8525.4653	0.0010
								7	6	8525.5644	0.0000
7	3	4	6	3	3	*1*	*1*	6	5	8525.4653	-0.0016
								8	7	8525.4761	-0.0002
								7	6	8525.5748	-0.0017
7	2	5	6	2	4	*0*	*0*	7	6	8672.0269	-0.0002
								8	7	8672.0486	0.0003
								6	5	8672.0562	-0.0011
7	2	5	6	2	4	*1*	*1*	7	6	8672.0486	0.0053
								8	7	8672.0650	0.0007
								6	5	8672.0756	0.0021
7	1	6	6	1	5	*0*	*0*	6	5	8815.3977	-0.0007
								8	7	8815.4034	-0.0003
								7	6	8815.4540	-0.0006
7	1	6	6	1	5	*1*	*1*	6	5	8815.4115	0.0004
								8	7	8815.4175	0.0011
								7	6	8815.4681	0.0008
8	1	8	7	1	7	*0*	*0*	9	8	9169.9495	-0.0003
								7	6	9169.9718	0.0000
								8	7	9169.9949	0.0002
8	1	8	7	1	7	*1*	*1*	9	8	9169.9551	0.0003
								7	6	9169.9769	0.0002
								8	7	9170.0004	0.0008
8	0	8	7	0	7	*0*	*0*	9	8	9377.2898	-0.0002

Table S15. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
8	0	8	7	0	7	*0*	*0*	7	6	9377.3035	0.0000
								8	7	9377.3979	-0.0003
8	0	8	7	0	7	*1*	*1*	9	8	9377.2948	-0.0007
								7	6	9377.3090	0.0000
								8	7	9377.4029	-0.0007
8	2	7	7	2	6	*0*	*0*	9	8	9642.9565	0.0020
								7	6	9642.9565	0.0011
								8	7	9643.0208	0.0014
8	2	7	7	2	6	*1*	*1*	7	6	9642.9634	-0.0028
								9	8	9642.9634	-0.0019
								8	7	9643.0278	-0.0024
8	3	6	7	3	5	*0*	*0*	7	6	9734.5101	-0.0123
								9	8	9734.5146	-0.0110
								8	7	9734.5860	-0.0141
8	3	6	7	3	5	*1*	*1*	7	6	9734.5330	-0.0027
								9	8	9734.5372	-0.0017
								8	7	9734.6119	-0.0015
8	3	5	7	3	4	*0*	*0*	7	6	9759.6907	0.0015
								9	8	9759.6907	0.0001
								8	7	9759.7472	0.0013
8	3	5	7	3	4	*1*	*1*	7	6	9759.7019	-0.0016
								9	8	9759.7019	-0.0030
								8	7	9759.7566	-0.0036
8	2	6	7	2	5	*0*	*0*	8	7	9960.1156	0.0065
								9	8	9960.1494	0.0042
								7	6	9960.1543	0.0004
8	2	6	7	2	5	*1*	*1*	8	7	9960.1244	-0.0038
								9	8	9960.1605	-0.0038
								7	6	9960.1691	-0.0039
8	1	7	7	1	6	*0*	*0*	7	6	10047.6740	-0.0005
								9	8	10047.6794	0.0004
								8	7	10047.7335	-0.0001
8	1	7	7	1	6	*1*	*1*	7	6	10047.6887	0.0009
								9	8	10047.6940	0.0018
								8	7	10047.7482	0.0013
9	1	9	8	1	8	*0*	*0*	10	9	10296.9370	0.0000
								8	7	10296.9537	-0.0005
								9	8	10296.9780	-0.0003
9	1	9	8	1	8	*1*	*1*	10	9	10296.9438	0.0015
								8	7	10296.9612	0.0017
								9	8	10296.9844	0.0008
9	0	9	8	0	8	*0*	*0*	10	9	10480.1602	-0.0052
								8	7	10480.1641	-0.0036
								9	8	10480.2552	-0.0059
9	0	9	8	0	8	*1*	*1*	10	9	10480.1710	0.0002
								8	7	10480.1752	0.0021
								9	8	10480.2677	0.0011
9	2	8	8	2	7	*0*	*0*	10	9	10830.4121	0.0004
								8	7	10830.4176	0.0020

Table S15. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
9	2	8	8	2	7	*0*	*0*	9	8	10830.4687	0.0023
9	2	8	8	2	7	*1*	*1*	10	9	10830.4208	-0.0025
								8	7	10830.4248	-0.0025
								9	8	10830.4761	-0.0019
9	3	7	8	3	6	*0*	*0*	8	7	10956.8916	0.0078
								10	9	10956.8916	0.0077
								9	8	10956.9430	0.0074
9	3	7	8	3	6	*1*	*1*	8	7	10956.9041	0.0053
								10	9	10956.9042	0.0054
								9	8	10956.9545	0.0039
9	3	6	8	3	5	*0*	*0*	10	9	11002.3852	-0.0004
								8	7	11002.3879	0.0000
								9	8	11002.4121	0.0016
9	3	6	8	3	5	*1*	*1*	10	9	11002.3992	-0.0034
								8	7	11002.4020	-0.0029
								9	8	11002.4270	-0.0004
9	2	7	8	2	6	*0*	*0*	9	8	11255.6345	-0.0060
								10	9	11255.6745	-0.0046
								8	7	11255.6852	-0.0009
9	2	7	8	2	6	*1*	*1*	9	8	11255.6648	0.0023
								10	9	11255.7020	0.0008
								8	7	11255.7096	0.0014
9	1	8	8	1	7	*0*	*0*	8	7	11267.1540	0.0000
								10	9	11267.1592	0.0010
								9	8	11267.2192	0.0001
9	1	8	8	1	7	*1*	*1*	8	7	11267.1677	0.0000
								10	9	11267.1742	0.0023
								9	8	11267.2327	-0.0001
10	1	10	9	1	9	*0*	*0*	11	10	11419.2460	-0.0001
								9	8	11419.2610	0.0006
								10	9	11419.2835	-0.0014
10	1	10	9	1	9	*1*	*1*	11	10	11419.2532	0.0015
								9	8	11419.2677	0.0018
								10	9	11419.2912	0.0007
10	0	10	9	0	9	*0*	*0*	11	10	11574.0023	-0.0028
								9	8	11574.0118	0.0000
								10	9	11574.0966	0.0023
10	0	10	9	0	9	*1*	*1*	11	10	11574.0118	0.0015
								9	8	11574.0157	-0.0011
								10	9	11574.1010	0.0015
10	2	9	9	2	8	*0*	*0*	11	10	12011.7987	-0.0027
								9	8	12011.8032	-0.0018
								10	9	12011.8537	0.0022
10	2	9	9	2	8	*1*	*1*	11	10	12011.8103	-0.0036
								9	8	12011.8181	0.0005
								10	9	12011.8675	0.0035
10	1	9	9	1	8	*0*	*0*	9	8	12471.2857	0.0000
								11	10	12471.2909	0.0011
								10	9	12471.3602	0.0018

Table S15. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	**Obs.**	**Obs. - Calc**
10	1	9	9	1	8	*1*	*1*	9	8	12471.2994	-0.0004
								11	10	12471.3049	0.0010
								10	9	12471.3723	-0.0002

Table S16. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{18}O_w$ isotologue of the complex *cis*-fa-w-a in the *v*=0 and *v*=1 vibrational states.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
5	1	5	4	1	4	*0*	*0*	6	5	5595.8735	0.0017
								4	3	5595.9280	0.0012
								5	4	5595.9496	0.0017
5	1	5	4	1	4	*1*	*1*	6	5	5595.8735	-0.0001
								4	3	5595.9280	-0.0007
								5	4	5595.9496	-0.0001
5	0	5	4	0	4	*0*	*0*	6	5	5805.5100	0.0014
								4	3	5805.5382	0.0016
								5	4	5805.6015	0.0000
5	0	5	4	0	4	*1*	*1*	6	5	5805.5100	0.0023
								4	3	5805.5382	0.0025
								5	4	5805.6015	0.0008
5	1	4	4	1	3	*0*	*0*	4	3	6140.8160	0.0020
								6	5	6140.8289	0.0013
								5	4	6140.8890	0.0019
5	1	4	4	1	3	*1*	*1*	4	3	6140.8007	-0.0035
								6	5	6140.8160	-0.0017
								5	4	6140.8753	-0.0019
6	1	6	5	1	5	*0*	*0*	7	6	6705.1332	0.0018
								5	4	6705.1753	0.0051
								6	5	6705.1918	0.0018
6	1	6	5	1	5	*1*	*1*	7	6	6705.1332	-0.0011
								5	4	6705.1753	0.0022
								6	5	6705.1918	-0.0011
6	0	6	5	0	5	*0*	*0*	7	6	6925.1636	0.0006
								5	4	6925.1825	0.0028
								6	5	6925.2713	0.0069
6	0	6	5	0	5	*1*	*1*	7	6	6925.1636	-0.0013
								5	4	6925.1825	0.0008
								6	5	6925.2713	0.0162
6	1	5	5	1	4	*0*	*0*	5	4	7356.0649	-0.0088
								7	6	7356.0845	0.0032
								6	5	7356.1271	-0.0052
6	1	5	5	1	4	*1*	*1*	5	4	7356.0649	0.0027
								7	6	7356.0845	0.0148
								6	5	7356.1271	0.0063
7	1	7	6	1	6	*0*	*0*	8	7	7809.7781	0.0055
								6	5	7809.8041	0.0029
								7	6	7809.8245	0.0021
7	1	7	6	1	6	*1*	*1*	8	7	7809.7781	0.0012
								6	5	7809.8041	-0.0013
								7	6	7809.8245	-0.0021
7	0	7	6	0	6	*0*	*0*	8	7	8026.6899	0.0021
								6	5	8026.7043	0.0054
								7	6	8026.7978	0.0044
7	0	7	6	0	6	*1*	*1*	8	7	8026.6899	-0.0034
								6	5	8026.7043	-0.0001

Table S16. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
7	0	7	6	0	6	1	1	7	6	8026.7978	-0.0011
7	1	6	6	1	5	0	0	6	5	8563.3699	-0.0062
								8	7	8563.3818	0.0003
								7	6	8563.4322	0.0001
7	1	6	6	1	5	1	1	6	5	8563.3616	-0.0017
								8	7	8563.3732	0.0045
								7	6	8563.4195	0.0002
8	1	8	7	1	7	0	0	9	8	8909.6348	0.0043
								7	6	8909.6556	0.0032
								8	7	8909.6766	0.0014
8	1	8	7	1	7	1	1	9	8	8909.6348	-0.0015
								7	6	8909.6556	-0.0026
								8	7	8909.6766	-0.0043
8	0	8	7	0	7	0	0	7	6	9111.6823	0.0049
								9	8	9111.7110	0.0044
								8	7	9111.7539	0.0072
8	0	8	7	0	7	1	1	7	6	9111.6823	-0.0061
								9	8	9111.7110	-0.0050
								8	7	9111.7539	-0.0083
8	1	7	7	1	6	0	0	7	6	9760.6721	-0.0015
								9	8	9760.6785	0.0004
								8	7	9760.7325	0.0000
8	1	7	7	1	6	1	1	7	6	9760.6574	-0.0031
								9	8	9760.6648	-0.0001
								8	7	9760.7184	-0.0008
9	1	9	8	1	8	0	0	10	9	10004.7437	0.0009
								8	7	10004.7589	-0.0010
								9	8	10004.7834	-0.0005
9	1	9	8	1	8	1	1	10	9	10004.7509	0.0005
								8	7	10004.7681	0.0004
								9	8	10004.7907	-0.0009
9	0	9	8	0	8	0	0	10	9	10183.6118	-0.0011
								8	7	10183.6567	-0.0012
9	0	9	8	0	8	1	1	10	9	10183.6221	-0.0039
								8	7	10183.6698	0.0003
								9	8	10183.7756	-0.0078
9	1	8	8	1	7	0	0	10	9	10945.6670	-0.0019
								8	7	10945.6670	0.0021
								9	8	10945.7322	0.0027
9	1	8	8	1	7	1	1	10	9	10945.6515	-0.0051
								8	7	10945.6515	-0.0010
								9	8	10945.7184	0.0012

Table S17. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{2}H_{w1}$ isotologue of the complex *cis*-fa-w-a in the ground vibrational state.

$J^{'}$	$K^{'}_{-1}$	$K^{'}_{+1}$	$J^{''}$	$K^{''}_{-1}$	$K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Obs. - Calc
3	1	3	2	1	2	4	3	3412.2721	0.0075
						2	1	3412.3853	-0.0019
3	2	2	2	2	1	3	3	3578.7658	-0.0051
3	1	2	2	1	1	2	1	3740.3271	0.0123
						2	1	3740.3271	0.0123
						4	3	3740.4325	-0.0046
4	1	4	3	1	3	5	4	4545.2555	-0.0093
4	0	4	3	0	3	5	4	4731.9995	0.0078
4	2	3	3	2	2	5	4	4768.6959	0.0083
4	2	2	3	2	1	5	4	4808.5554	-0.0161
5	1	5	4	1	4	6	5	5674.6708	-0.0035
5	0	5	4	0	4	6	5	5886.0325	-0.0036
5	2	4	4	2	3	6	5	5955.8849	0.0026
5	2	3	4	2	2	4	3	6034.6806	0.0099
						6	5	6034.6806	0.0008
5	1	4	4	1	3	6	5	6219.7907	0.0073
6	1	6	5	1	5	5	4	6799.9847	0.0141
						6	5	6799.9847	-0.0051
6	0	6	5	0	5	7	6	7022.7481	0.0025
						5	4	7022.7481	-0.0143
6	2	5	5	2	4	7	6	7139.7167	-0.0052
						5	4	7139.7167	-0.0033
6	2	4	5	2	3	5	4	7274.7285	-0.0009
						7	6	7274.7285	0.0047
						6	5	7274.7285	-0.0106
6	1	5	5	1	4	5	4	7451.2131	-0.0065
						7	6	7451.2131	-0.0139
7	1	7	6	1	6	8	7	7920.6782	0.0190
						6	5	7920.6782	-0.0095

Table S18. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{2}H_{w2}$ isotologue of the complex *cis*-fa-w-a in the ground vibrational state.

$J^{'}$	$K^{'}_{-1}$	$K^{'}_{+1}$	$J^{''}$	$K^{''}_{-1}$	$K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Obs. - Calc
3	1	3	2	1	2	4	3	3389.9335	-0.0052
						3	2	3390.1694	0.0057
3	1	2	2	1	1	4	3	3721.2498	-0.0052
						3	2	3721.4416	0.0082
5	1	5	4	1	4	5	4	5636.9765	-0.0103
						4	3	5636.9765	0.0108
5	0	5	4	0	4	6	5	5848.0544	-0.0176
						5	4	5848.1584	-0.0073
5	2	4	4	2	3	6	5	5921.0801	0.0093
						5	4	5921.2512	0.0150
5	2	3	4	2	2	6	5	6003.4192	-0.0179
						4	3	6003.4192	-0.0090
						5	4	6003.5097	-0.0105
5	1	4	4	1	3	6	5	6187.1235	0.0163
6	1	6	5	1	5	7	6	6754.2226	0.0106
						6	5	6754.2655	-0.0051
						5	4	6754.2655	0.0148
6	0	6	5	0	5	5	4	6975.5716	-0.0043
						7	6	6975.5716	0.0123
						6	5	6975.6493	-0.0119
6	2	5	5	2	4	7	6	7097.6049	0.0000
						5	4	7097.6049	0.0019
6	2	4	5	2	3	5	4	7238.5179	-0.0010
						7	6	7238.5179	0.0048
						6	5	7238.5179	-0.0087
6	1	5	5	1	4	7	6	7411.3690	-0.0041
						5	4	7411.3690	0.0033

Table S19. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{2}H_{1}$ isotologue of the complex *cis*-fa-w-a in the ground vibrational state.

$J^{'}$	$K^{'}_{-1}$	$K^{'}_{+1}$	$J^{''}$	$K^{''}_{-1}$	$K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Obs. - Calc
3	0	3	2	0	2	4	3	3609.9691	0.0223
						3	2	3609.9691	-0.0534
3	1	2	2	1	1	4	3	3794.4802	0.0097
						3	2	3794.6517	0.0029
4	0	4	3	0	3	3	2	4793.3353	-0.0246
						5	4	4793.3353	0.0276
5	1	5	4	1	4	6	5	5744.3229	0.0035
5	0	5	4	0	4	6	5	5960.4173	-0.0064
5	2	4	4	2	3	4	3	6035.8110	-0.0083
						5	4	6036.0051	0.0024
5	2	3	4	2	2	4	3	6120.9097	-0.0116
						5	4	6121.0147	0.0016
5	1	4	4	1	3	6	5	6308.6546	0.0318
						5	4	6308.6546	-0.0280
6	1	6	5	1	5	6	5	6882.8118	-0.0231
						5	4	6882.8118	-0.0029
						7	6	6882.8118	0.0357
6	0	6	5	0	5	6	5	7109.0658	-0.0686
						5	4	7109.0658	0.0171
						7	6	7109.0658	0.0337
6	2	5	5	2	4	7	6	7235.0719	0.0043
						5	4	7235.0719	0.0062
						6	5	7235.1740	-0.0007
6	2	4	5	2	3	7	6	7380.6010	0.0066
						6	5	7380.6010	-0.0064
						5	4	7380.6010	0.0007
6	1	5	5	1	4	7	6	7556.7612	0.0215
						6	5	7556.7612	-0.0301

Table S20. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the parent species of the complex *trans*-fa-w-b in the ground vibrational state.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
5	0	5	4	0	4	6	5	5063.4394	0.0000
						4	3	5063.4677	0.0007
						5	4	5063.4885	-0.0006
5	2	4	4	2	3	4	3	5077.6948	0.0027
						6	5	5077.7068	0.0001
						5	4	5077.8571	0.0114
5	2	3	4	2	2	4	3	5093.8049	-0.0014
						6	5	5093.8185	0.0020
						5	4	5093.9140	-0.0014
5	1	4	4	1	3	4	3	5231.2395	-0.0003
						6	5	5231.2659	0.0000
						5	4	5231.3035	0.0006
6	1	6	5	1	5	7	6	5902.7788	-0.0002
						6	5	5902.8248	-0.0009
						5	4	5902.8248	0.0008
6	0	6	5	0	5	7	6	6067.3474	0.0000
						5	4	6067.3638	-0.0005
						6	5	6067.4024	-0.0002
6	2	5	5	2	4	5	4	6091.7820	-0.0004
						7	6	6091.7820	-0.0012
						6	5	6091.8696	-0.0002
6	2	4	5	2	3	7	6	6119.8891	-0.0012
						5	4	6119.8947	0.0006
						6	5	6119.9285	-0.0005
6	1	5	5	1	4	5	4	6275.1760	-0.0003
						7	6	6275.1916	-0.0001
						6	5	6275.2192	-0.0002
7	1	7	6	1	6	8	7	6883.7109	-0.0002
						6	5	6883.7434	-0.0006
						7	6	6883.7492	0.0002
7	0	7	6	0	6	8	7	7066.5913	-0.0001
						6	5	7066.6023	-0.0002
						7	6	7066.6525	-0.0002
7	2	6	6	2	5	8	7	7105.0426	-0.0011
						6	5	7105.0463	-0.0006
						7	6	7105.1022	-0.0017
7	2	5	6	2	4	8	7	7149.8078	0.0030
						7	6	7149.8124	0.0033
						6	5	7149.8124	0.0004
7	1	6	6	1	5	6	5	7317.7749	0.0000
						8	7	7317.7853	0.0000
						7	6	7317.8094	-0.0003
8	1	8	7	1	7	9	8	7863.4030	0.0000
						7	6	7863.4272	-0.0008
						8	7	7863.4363	0.0003
8	0	8	7	0	7	9	8	8060.5651	-0.0004
						7	6	8060.5758	0.0025

Table S20. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
8	0	8	7	0	7	8	7	8060.6322	-0.0005
8	2	7	7	2	6	9	8	8117.3560	-0.0012
						7	6	8117.3607	-0.0007
						8	7	8117.4019	-0.0010
8	2	6	7	2	5	8	7	8184.0128	-0.0009
						9	8	8184.0293	-0.0014
						7	6	8184.0381	-0.0008
8	1	7	7	1	6	7	6	8358.7664	-0.0001
						9	8	8358.7745	0.0002
						8	7	8358.7978	-0.0002
9	1	9	8	1	8	10	9	8841.7397	0.0004
						8	7	8841.7582	-0.0008
						9	8	8841.7696	0.0001
9	0	9	8	0	8	10	9	9048.7998	-0.0007
						8	7	9048.8056	-0.0001
						9	8	9048.8727	-0.0003
9	2	8	8	2	7	10	9	9128.5917	-0.0006
						8	7	9128.5965	0.0000
						9	8	9128.6286	-0.0010
9	2	7	8	2	6	9	8	9222.8681	-0.0007
						10	9	9222.8992	-0.0012
						8	7	9222.9085	0.0001
9	1	8	8	1	7	8	7	9397.8554	-0.0004
						10	9	9397.8622	0.0002
						9	8	9397.8865	-0.0002
10	1	10	9	1	9	11	10	9818.6272	0.0005
						9	8	9818.6424	0.0000
						10	9	9818.6558	0.0006
10	0	10	9	0	9	11	10	10031.0100	-0.0007
						9	8	10031.0149	0.0005
						10	9	10031.0870	-0.0005
10	2	9	9	2	8	11	10	10138.6177	-0.0007
						9	8	10138.6227	0.0004
						10	9	10138.6503	-0.0004
10	2	8	9	2	7	10	9	10266.5177	0.0000
						11	10	10266.5583	-0.0007
						9	8	10266.5662	-0.0001
10	1	9	9	1	8	9	8	10434.7195	-0.0004
						11	10	10434.7257	0.0006
						10	9	10434.7518	0.0000
11	1	11	10	1	10	12	11	10793.9948	0.0004
						10	9	10794.0083	0.0009
						11	10	10794.0224	0.0004
11	0	11	10	0	10	12	11	11007.1313	-0.0010
						10	9	11007.1354	0.0003
						11	10	11007.2120	-0.0003
11	2	10	10	2	9	12	11	11147.3068	0.0000
						10	9	11147.3111	0.0009
						11	10	11147.3365	0.0003

Table S20. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
11	2	9	10	2	8	11	10	11314.8786	0.0000
						12	11	11314.9267	0.0002
						10	9	11314.9337	0.0007
11	1	10	10	1	9	10	9	11469.0064	0.0002
						12	11	11469.0119	0.0014
						11	10	11469.0402	0.0005
1	1	1	0	0	0	2	1	4571.7271	0.0070
						1	1	4572.2146	-0.0138
2	1	2	1	0	1	3	2	5525.4275	-0.0009
						1	0	5525.6275	-0.0050
						2	1	5526.0275	0.0138
3	1	3	2	0	2	4	3	6448.4162	0.0021
						3	2	6449.1461	-0.0014
4	1	4	3	0	3	5	4	7341.6784	0.0001
						4	3	7342.4659	-0.0019

Table S21. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{18}O_w$ isotologue of the complex *trans*-fa-w-b in the ground vibrational state.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
6	1	5	5	1	4	5	4	5985.3502	0.0013
						7	6	5985.3652	0.0010
						6	5	5985.3887	-0.0018
7	1	7	6	1	6	8	7	6584.0085	-0.0006
						6	5	6584.0386	-0.0036
						7	6	6584.0462	0.0002
7	0	7	6	0	6	8	7	6753.7849	0.0002
						6	5	6753.7962	0.0001
						7	6	6753.8410	0.0000
7	2	6	6	2	5	6	5	6785.6699	-0.0029
						8	7	6785.6699	0.0003
						7	6	6785.7258	-0.0030
7	2	5	6	2	4	8	7	6822.7791	-0.0031
						7	6	6822.7902	-0.0020
						6	5	6822.7902	-0.0006
7	1	6	6	1	5	6	5	6980.2196	-0.0006
						8	7	6980.2251	-0.0054
						7	6	6980.2591	0.0055
8	1	8	7	1	7	9	8	7521.4961	-0.0001
						7	6	7521.5190	-0.0023
						8	7	7521.5286	0.0006
8	0	8	7	0	7	9	8	7705.6600	-0.0001
						7	6	7705.6676	0.0010
						8	7	7705.7220	0.0000
8	1	8	7	0	7	7	6	10401.3640	0.0002
						9	8	10401.4481	0.0027
						8	7	10402.2184	0.0002
9	1	9	8	0	8	8	7	11153.5542	-0.0034
						10	9	11153.6271	0.0013
						9	8	11154.3696	0.0038
10	0	10	9	1	9	10	9	7093.0165	0.0027
						11	10	7093.6167	0.0012
						9	8	7093.6959	0.0013

Table S22. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{2}H_{w1}$ isotologue of the complex *trans*-fa-w-b in the ground vibrational state.

$J^{'}$	$K^{'}_{-1}$	$K^{'}_{+1}$	$J^{''}$	$K^{''}_{-1}$	$K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Obs. - Calc
5	1	5	4	1	4	6	5	4846.0096	0.0103
6	0	6	5	0	5	7	6	5973.7691	-0.0162
6	2	5	5	2	4	7	6	5996.9626	0.0029
						5	4	5996.9627	0.0038
						6	5	5997.0500	0.0040
6	2	4	5	2	3	7	6	6023.6091	-0.0078
						5	4	6023.6091	-0.0115
6	1	5	5	1	4	7	6	6175.4227	0.0014
7	1	7	6	1	6	8	7	6779.3499	0.0088
7	0	7	6	0	6	8	7	6958.0506	0.0063
						6	5	6958.0507	-0.0046
7	2	6	6	2	5	6	5	6994.5276	0.0026
						8	7	6994.5276	0.0058
7	2	5	6	2	4	8	7	7036.9874	0.0039
						7	6	7036.9874	-0.0014
						6	5	7036.9876	-0.0029
7	1	6	6	1	5	7	6	7201.5874	0.0030
8	1	8	7	1	7	9	8	7744.2958	-0.0103

Table S23. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the parent species of the complex *trans*-fa-w-c in the *v*=0 and *v*=1 vibrational states.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
4	1	4	3	1	3	*0*	*0*	5	4	5163.4679	0.0002
								4	3	5163.6481	0.0000
4	1	4	3	1	3	*1*	*1*	5	4	5163.5819	0.0012
								3	2	5163.6596	0.0000
								4	3	5163.7597	-0.0014
4	0	4	3	0	3	*0*	*0*	5	4	5300.0497	0.0012
								3	2	5300.0942	0.0000
								4	3	5300.3061	0.0010
4	0	4	3	0	3	*1*	*1*	5	4	5300.0424	-0.0019
								3	2	5300.0887	-0.0014
								4	3	5300.2994	-0.0015
4	2	3	3	2	2	*0*	*0*	3	2	5886.0755	-0.0004
								5	4	5886.1628	-0.0003
								4	3	5886.5024	0.0008
4	2	3	3	2	2	*1*	*1*	3	2	5886.0111	0.0005
								5	4	5886.0965	-0.0012
								4	3	5886.4363	0.0000
4	2	2	3	2	1	*0*	*0*	3	2	6541.1750	0.0031
								5	4	6541.2462	-0.0004
								4	3	6541.3479	0.0000
4	2	2	3	2	1	*1*	*1*	3	2	6541.0475	-0.0011
								5	4	6541.1237	0.0002
								4	3	6541.2252	0.0005
4	1	3	3	1	2	*0*	*0*	3	2	6375.8713	0.0007
								5	4	6375.9477	-0.0001
								4	3	6376.1892	0.0009
4	1	3	3	1	2	*1*	*1*	3	2	6375.6056	0.0004
								5	4	6375.6815	-0.0010
								4	3	6375.9236	0.0005
5	1	5	4	1	4	*0*	*0*	6	5	6365.5694	0.0005
								4	3	6365.6241	0.0012
								5	4	6365.7040	-0.0013
5	1	5	4	1	4	*1*	*1*	6	5	6365.7240	0.0012
								4	3	6365.7794	0.0026
								5	4	6365.8606	0.0012
5	0	5	4	0	4	*0*	*0*	6	5	6432.0353	-0.0004
								4	3	6432.0777	0.0003
								5	4	6432.2155	0.0007
5	0	5	4	0	4	*1*	*1*	6	5	6432.1150	0.0011
								4	3	6432.1569	0.0014
								5	4	6432.2931	0.0003
5	2	4	4	2	3	*0*	*0*	4	3	7248.0508	-0.0011
								6	5	7248.0831	0.0008
								5	4	7248.3203	0.0007
5	2	4	4	2	3	*1*	*1*	4	3	7247.9648	-0.0005
								6	5	7247.9938	-0.0018
								5	4	7248.2322	-0.0008

Table S23. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
5	2	3	4	2	2	*0*	*0*	4	3	8244.1638	0.0009
								6	5	8244.2032	-0.0002
								5	4	8244.2911	0.0001
5	2	3	4	2	2	*1*	*1*	4	3	8243.9099	0.0006
								6	5	8243.9497	0.0000
								5	4	8244.0380	0.0006
5	3	3	4	3	2	*0*	*0*	4	3	7625.5025	0.0054
								6	5	7625.5751	-0.0008
								5	4	7625.8597	-0.0008
5	3	3	4	3	2	*1*	*1*	4	3	7625.3997	-0.0007
								6	5	7625.4772	-0.0021
								5	4	7625.7648	0.0008
5	3	2	4	3	1	*0*	*0*	4	3	7910.1360	0.0004
								6	5	7910.1857	-0.0020
								5	4	7910.3079	0.0003
5	3	2	4	3	1	*1*	*1*	4	3	7910.1206	0.0003
								6	5	7910.1714	-0.0009
								5	4	7910.2927	0.0005
5	1	4	4	1	3	*0*	*0*	4	3	7711.4550	-0.0001
								6	5	7711.5068	-0.0009
								5	4	7711.7860	0.0009
5	1	4	4	1	3	*1*	*1*	4	3	7711.0999	0.0019
								6	5	7711.1503	-0.0002
								5	4	7711.4275	-0.0004
6	1	6	5	1	5	*0*	*0*	7	6	7547.0179	0.0005
								5	4	7547.0579	0.0005
								6	5	7547.1234	-0.0008
6	1	6	5	1	5	*1*	*1*	7	6	7547.2242	0.0007
								5	4	7547.2628	-0.0007
								6	5	7547.3308	0.0003
6	0	6	5	0	5	*0*	*0*	7	6	7574.7954	0.0001
								5	4	7574.8324	0.0009
								6	5	7574.9218	0.0022
6	0	6	5	0	5	*1*	*1*	7	6	7574.9632	0.0009
								5	4	7574.9975	-0.0009
								6	5	7575.0859	-0.0006
6	2	5	5	2	4	*0*	*0*	5	4	8550.8346	0.0001
								7	6	8550.8474	0.0000
								6	5	8551.0433	0.0014
6	2	5	5	2	4	*1*	*1*	5	4	8550.7312	-0.0010
								7	6	8550.7447	-0.0004
								6	5	8550.9395	-0.0001
6	2	4	5	2	3	*0*	*0*	5	4	9833.4566	-0.0002
								7	6	9833.4903	-0.0001
								6	5	9833.6193	-0.0008
6	2	4	5	2	3	*1*	*1*	5	4	9833.0442	0.0011
								7	6	9833.0768	0.0001
								6	5	9833.2069	0.0004
6	1	5	5	1	4	*0*	*0*	5	4	8896.6194	0.0016

Table S23. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
6	1	5	5	1	4	*0*	*0*	7	6	8896.6534	0.0002
								6	5	8896.9357	0.0003
								5	4	8896.2220	0.0039
6	1	5	5	1	4	*1*	*1*	7	6	8896.2516	-0.0018
								6	5	8896.5335	-0.0021
7	1	7	6	1	6	*0*	*0*	8	7	8717.7449	0.0002
								6	5	8717.7754	-0.0006
								7	6	8717.8260	-0.0034
7	1	7	6	1	6	*1*	*1*	8	7	8718.0123	0.0004
								6	5	8718.0431	-0.0001
								7	6	8718.0964	-0.0002
7	0	7	6	0	6	*0*	*0*	8	7	8728.3679	0.0003
								6	5	8728.3978	0.0000
								7	6	8728.4589	0.0003
7	0	7	6	0	6	*1*	*1*	8	7	8728.6168	-0.0003
								6	5	8728.6477	0.0003
								7	6	8728.7083	0.0002
7	2	6	6	2	5	*0*	*0*	6	5	9800.7796	-0.0006
								8	7	9800.7859	0.0003
								7	6	9800.9525	-0.0015
7	2	6	6	2	5	*1*	*1*	6	5	9800.6749	-0.0018
								8	7	9800.6824	0.0003
								7	6	9800.8520	0.0014
7	1	6	6	1	5	*0*	*0*	6	5	10005.1477	0.0011
								8	7	10005.1659	0.0004
								7	6	10005.4052	0.0007
7	1	6	6	1	5	*1*	*1*	6	5	10004.8039	0.0025
								8	7	10004.8215	0.0012
								7	6	10005.0594	0.0001
8	1	8	7	1	7	*0*	*0*	9	8	9883.6862	0.0003
								7	6	9883.7102	-0.0010
								8	7	9883.7537	-0.0001
8	1	8	7	1	7	*1*	*1*	9	8	9884.0200	0.0005
								7	6	9884.0447	-0.0001
								8	7	9884.0873	-0.0001
8	0	8	7	0	7	*0*	*0*	9	8	9887.5264	-0.0002
								7	6	9887.5496	-0.0021
								8	7	9887.5954	-0.0013
8	0	8	7	0	7	*1*	*1*	9	8	9887.8539	0.0010
								7	6	9887.8779	0.0000
								8	7	9887.9232	0.0002
8	2	7	7	2	6	*0*	*0*	7	6	11011.1803	0.0010
								9	8	11011.1803	-0.0002
								8	7	11011.3269	0.0000
8	2	7	7	2	6	*1*	*1*	7	6	11011.0962	0.0013
								9	8	11011.0962	0.0000
								8	7	11011.2424	-0.0001
8	1	7	7	1	6	*0*	*0*	7	6	11112.2307	-0.0023
								9	8	11112.2409	0.0005

Table S23. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
8	1	7	7	1	6	*0*	*0*	8	7	11112.4277	0.0024
8	1	7	7	1	6	*1*	*1*	7	6	11111.9955	-0.0022
								9	8	11112.0089	0.0038
								8	7	11112.1897	-0.0002
4	0	4	3	1	3	*0*	*0*	5	4	5052.7499	-0.0003
								3	2	5052.8475	0.0006
								4	3	5052.8614	-0.0002
4	0	4	3	1	3	*1*	*1*	5	4	5053.0077	0.0000
								3	2	5053.1029	-0.0015
								4	3	5053.1198	0.0004
5	0	5	4	1	4	*0*	*0*	6	5	6321.3178	-0.0005
								4	3	6321.3783	0.0006
								5	4	6321.4281	-0.0001
5	0	5	4	1	4	*1*	*1*	6	5	6321.5403	-0.0006
								4	3	6321.6027	0.0023
								5	4	6321.6509	0.0000
6	0	6	5	1	5	*0*	*0*	7	6	7530.5450	0.0002
								5	4	7530.5863	0.0000
								6	5	7530.6421	-0.0003
6	0	6	5	1	5	*1*	*1*	7	6	7530.7801	-0.0003
								5	4	7530.8221	0.0000
								6	5	7530.8784	0.0002
7	0	7	6	1	6	*0*	*0*	8	7	8711.8950	0.0000
								6	5	8711.9230	-0.0038
								7	6	8711.9766	-0.0001
7	0	7	6	1	6	*1*	*1*	8	7	8712.1746	0.0005
								6	5	8712.2070	0.0010
								7	6	8712.2558	0.0000
8	0	8	7	1	7	*0*	*0*	9	8	9881.6776	0.0006
								7	6	9881.7035	0.0009
								8	7	9881.7437	-0.0003
8	0	8	7	1	7	*1*	*1*	9	8	9882.0153	0.0001
								7	6	9882.0408	0.0001
								8	7	9882.0821	0.0000
3	1	3	2	0	2	*0*	*0*	4	3	4392.6805	0.0002
								3	2	4393.1389	0.0003
3	1	3	2	0	2	*1*	*1*	4	3	4392.3725	-0.0011
								2	1	4392.4003	0.0039
								3	2	4392.8306	-0.0013
4	1	4	3	0	3	*0*	*0*	5	4	5410.7663	0.0004
								3	2	5410.7933	-0.0006
								4	3	5411.0921	0.0006
4	1	4	3	0	3	*1*	*1*	5	4	5410.6151	-0.0021
								3	2	5410.6414	-0.0038
								4	3	5410.9411	-0.0016
5	1	5	4	0	4	*0*	*0*	6	5	6476.2859	-0.0004
								4	3	6476.3219	-0.0005
								5	4	6476.4904	-0.0014
5	1	5	4	0	4	*1*	*1*	6	5	6476.2963	0.0006

Table S23. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
5	1	5	4	0	4	*1*	*1*	4	3	6476.3322	0.0003
								5	4	6476.5014	0.0002
6	1	6	5	0	5	*0*	*0*	7	6	7591.2699	0.0020
								5	4	7591.3030	0.0005
								6	5	7591.4018	0.0004
6	1	6	5	0	5	*1*	*1*	7	6	7591.4068	0.0015
								5	4	7591.4394	-0.0005
								6	5	7591.5376	-0.0011
7	1	7	6	0	6	*0*	*0*	8	7	8734.2179	0.0006
								6	5	8734.2460	-0.0010
								7	6	8734.3118	0.0005
7	1	7	6	0	6	*1*	*1*	8	7	8734.4549	0.0000
								6	5	8734.4839	-0.0007
								7	6	8734.5492	0.0003
8	1	8	7	0	7	*0*	*0*	9	8	9889.5354	0.0000
								7	6	9889.5600	-0.0004
								8	7	9889.6073	0.0007
8	1	8	7	0	7	*1*	*1*	9	8	9889.8570	-0.0001
								7	6	9889.8833	0.0011
								8	7	9889.9288	0.0005
5	1	4	4	2	3	*0*	*0*	6	5	6523.2351	-0.0013
								4	3	6523.2484	-0.0034
								5	4	6523.2484	-0.0011
5	1	4	4	2	3	*1*	*1*	6	5	6523.9816	-0.0013
								4	3	6523.9966	-0.0017
								5	4	6523.9966	0.0004
6	1	5	5	2	4	*0*	*0*	7	6	8171.8074	0.0000
								5	4	8171.8180	0.0002
								6	5	8171.8656	0.0003
6	1	5	5	2	4	*1*	*1*	7	6	8172.2400	-0.0007
								5	4	8172.2510	0.0000
								6	5	8172.2987	0.0000
7	1	6	6	2	5	*0*	*0*	8	7	9626.1252	-0.0004
								6	5	9626.1303	0.0005
								7	6	9626.2282	0.0003
7	1	6	6	2	5	*1*	*1*	8	7	9626.3157	-0.0002
								6	5	9626.3209	0.0007
								7	6	9626.4184	0.0001
8	1	7	7	2	6	*0*	*0*	9	8	10937.5780	-0.0023
								7	6	10937.5813	-0.0013
								8	7	10937.6995	0.0003
8	1	7	7	2	6	*1*	*1*	9	8	10937.6365	-0.0024
								7	6	10937.6411	0.0000
								8	7	10937.7581	0.0004
3	2	2	2	1	1	*0*	*0*	2	1	6568.7378	-0.0023
								4	3	6568.9768	0.0038
								3	2	6569.3919	0.0006
3	2	2	2	1	1	*1*	*1*	2	1	6567.2524	-0.0018
								4	3	6567.4837	-0.0033

Table S23. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
3	2	2	2	1	1	*1*	*1*	3	2	6567.9051	-0.0002
4	2	3	3	1	2	*0*	*0*	3	2	7564.0725	-0.0012
								5	4	7564.2224	0.0032
								4	3	7564.7259	0.0021
4	2	3	3	1	2	*1*	*1*	3	2	7562.7040	-0.0008
								5	4	7562.8499	-0.0002
								4	3	7563.3549	0.0000
5	2	4	4	1	3	*0*	*0*	4	3	8436.2561	0.0009
								6	5	8436.3531	-0.0003
								5	4	8436.8561	0.0010
5	2	4	4	1	3	*1*	*1*	4	3	8435.0635	-0.0014
								6	5	8435.1614	-0.0018
								5	4	8435.6614	-0.0034
3	3	0	2	2	1	*0*	*0*	3	2	8851.3200	-0.0012
								2	1	8851.5800	-0.0003
								4	3	8851.6116	-0.0015
3	3	0	2	2	1	*1*	*1*	3	2	8848.6699	0.0015
								2	1	8848.9304	0.0028
								4	3	8848.9619	0.0015
3	3	1	2	2	0	*0*	*0*	2	1	8745.0144	0.0046
								3	2	8745.1598	-0.0002
								4	3	8745.1837	-0.0007
3	3	1	2	2	0	*1*	*1*	2	1	8742.3427	-0.0017
								3	2	8742.4951	0.0003
								4	3	8742.5199	0.0006
4	3	2	3	2	1	*0*	*0*	3	2	10053.4683	-0.0034
								5	4	10053.5535	-0.0014
								4	3	10053.6861	-0.0023
4	3	2	3	2	1	*1*	*1*	3	2	10050.7926	0.0023
								5	4	10050.8735	0.0000
								4	3	10051.0057	-0.0014

Table S24. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{18}O_w$ isotologue of the complex *trans*-fa-w-c in the *v*=0 and *v*=1 vibrational states.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	Obs.	Obs. - Calc
7	1	7	6	1	6	*0*	*0*	7	6	8449.1341	0.0001
								6	5	8449.0797	-0.0008
								8	7	8449.0503	0.0011
7	1	7	6	1	6	*1*	*1*	7	6	8449.4326	0.0002
								6	5	8449.3771	-0.0017
								8	7	8449.3478	0.0003
7	0	7	6	0	6	*0*	*0*	7	6	8459.7625	0.0009
								6	5	8459.6993	-0.0012
								8	7	8459.6716	0.0012
7	0	7	6	0	6	*1*	*1*	7	6	8460.0369	-0.0001
								6	5	8459.9757	-0.0002
								8	7	8459.9463	0.0005
5	0	5	4	1	4	*0*	*0*	5	4	6124.9210	-0.0009
								4	3	6124.8725	0.0001
								6	5	6124.8155	0.0026
5	0	5	4	1	4	*1*	*1*	5	4	6125.1972	-0.0003
								4	3	6125.1483	0.0003
								6	5	6125.0892	0.0007
5	1	5	4	0	4	*0*	*0*	5	4	6278.8699	0.0002
								6	5	6278.6620	-0.0008
								4	3	6278.6979	-0.0007
5	1	5	4	0	4	*1*	*1*	5	4	6278.8720	-0.0037
								6	5	6278.6701	0.0011
								4	3	6278.7052	0.0004
6	0	6	5	1	5	*0*	*0*	6	5	7297.8142	-0.0014
								5	4	7297.7599	0.0000
								7	6	7297.7175	-0.0008
6	0	6	5	1	5	*1*	*1*	6	5	7298.0915	-0.0006
								5	4	7298.0373	0.0009
								7	6	7297.9946	-0.0001
6	1	6	5	0	5	*0*	*0*	6	5	7358.5009	0.0011
								5	4	7358.4003	0.0002
								7	6	7358.3662	0.0006
6	1	6	5	0	5	*1*	*1*	6	5	7358.6517	0.0023
								5	4	7358.5493	-0.0002
								7	6	7358.5167	0.0015
7	0	7	6	1	6	*0*	*0*	7	6	8443.2265	-0.0012
								6	5	8443.1763	-0.0016
								8	7	8443.1460	-0.0001
7	0	7	6	1	6	*1*	*1*	7	6	8443.5400	-0.0019
								6	5	8443.4911	-0.0009
								8	7	8443.4604	0.0001
7	1	7	6	0	6	*0*	*0*	7	6	8465.6676	-0.0001
								6	5	8465.6038	0.0006
								8	7	8465.5744	0.0010
7	1	7	6	0	6	*1*	*1*	7	6	8465.9284	0.0010
								6	5	8465.8627	0.0000

Table S24. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	v'	v''	F'	F''	**Obs.**	**Obs. - Calc**
7	1	7	6	0	6	*1*	*1*	8	7	8465.8337	0.0006

Table S25. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the parent species of the complex *cis*-fa-w_2-a in the ground vibrational state.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
6	1	6	5	1	5	7	6	5100.0812	0.0001
						5	4	5100.1182	0.0000
						6	5	5100.1399	-0.0003
6	0	6	5	0	5	7	6	5268.0416	0.0003
						5	4	5268.0561	0.0001
						6	5	5268.1513	0.0002
6	2	5	5	2	4	5	4	5379.1364	0.0002
						7	6	5379.1386	0.0001
						6	5	5379.2427	0.0006
6	3	4	5	3	3	5	4	5415.0931	0.0003
						7	6	5415.1210	0.0006
						6	5	5415.2897	0.0005
6	3	3	5	3	2	5	4	5420.9569	-0.0005
						7	6	5420.9835	-0.0001
						6	5	5421.1422	-0.0002
6	2	4	5	2	3	6	5	5507.6041	-0.0010
						7	6	5507.6041	0.0004
						5	4	5507.6108	0.0011
6	1	5	5	1	4	5	4	5630.7534	0.0004
						7	6	5630.7628	0.0008
						6	5	5630.8157	-0.0003
7	1	7	6	1	6	8	7	5938.3481	0.0001
						6	5	5938.3743	-0.0010
						7	6	5938.3996	0.0007
7	0	7	6	0	6	8	7	6099.0136	-0.0003
						6	5	6099.0237	0.0000
						7	6	6099.1256	-0.0003
7	2	6	6	2	5	8	7	6265.9080	-0.0006
						6	5	6265.9113	0.0000
						7	6	6265.9849	-0.0006
7	3	5	6	3	4	6	5	6322.0057	-0.0006
						8	7	6322.0165	0.0000
						7	6	6322.1213	0.0001
7	3	4	6	3	3	6	5	6335.0954	-0.0001
						8	7	6335.1043	0.0003
						7	6	6335.1920	-0.0002
7	2	5	6	2	4	7	6	6462.5888	0.0005
						8	7	6462.6165	-0.0002
						6	5	6462.6266	0.0012
7	1	6	6	1	5	6	5	6551.2015	-0.0004
						8	7	6551.2095	0.0009
						7	6	6551.2647	0.0005
8	1	8	7	1	7	9	8	6772.4113	0.0013
						7	6	6772.4276	-0.0033
						8	7	6772.4569	0.0008
8	0	8	7	0	7	9	8	6916.8738	0.0010
						7	6	6916.8820	0.0005

Table S25. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
8	0	8	7	0	7	8	7	6916.9806	-0.0006
8	2	7	7	2	6	9	8	7148.2585	-0.0010
						7	6	7148.2635	0.0007
						8	7	7148.3237	0.0006
8	3	6	7	3	5	7	6	7229.6881	-0.0005
						9	8	7229.6930	0.0011
						8	7	7229.7603	-0.0006
8	3	5	7	3	4	9	8	7255.5449	0.0000
						7	6	7255.5449	0.0008
						8	7	7255.5907	0.0010
8	2	6	7	2	5	8	7	7425.9782	0.0000
						9	8	7426.0157	-0.0013
						7	6	7426.0251	0.0003
8	1	7	7	1	6	7	6	7461.8923	-0.0004
						9	8	7461.8991	0.0006
						8	7	7461.9606	0.0008
9	1	9	8	1	8	10	9	7602.3976	0.0000
						8	7	7602.4142	-0.0001
						9	8	7602.4397	-0.0005
9	0	9	8	0	8	10	9	7725.3539	0.0000
						8	7	7725.3618	0.0010
						9	8	7725.4529	0.0007
9	2	8	8	2	7	10	9	8025.6610	-0.0019
						8	7	8025.6653	-0.0010
						9	8	8025.7184	-0.0006
9	3	7	8	3	6	10	9	8137.5319	-0.0004
						8	7	8137.5319	-0.0002
						9	8	8137.5811	0.0001
9	1	8	8	1	7	8	7	8360.5691	-0.0015
						10	9	8360.5774	0.0015
						9	8	8360.6452	0.0000
9	2	7	8	2	6	9	8	8393.2138	-0.0003
						10	9	8393.2505	-0.0002
						8	7	8393.2560	-0.0005
10	1	10	9	1	9	11	10	8428.6025	0.0001
						9	8	8428.6165	0.0006
						10	9	8428.6408	-0.0013
10	0	10	9	0	9	11	10	8528.4388	-0.0002
						9	8	8528.4477	0.0017
						10	9	8528.5254	0.0000
10	2	9	9	2	8	11	10	8897.6672	0.0002
						9	8	8897.6710	0.0008
						10	9	8897.7194	0.0002
10	4	7	9	4	6	9	8	9042.2793	-0.0002
						11	10	9042.2827	0.0003
						10	9	9042.3405	-0.0001
10	3	8	9	3	7	11	10	9044.7640	0.0000
						9	8	9044.7640	-0.0009
						10	9	9044.8005	-0.0003

Table S25. Continued.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
10	3	7	9	3	6	10	9	9122.4572	0.0001
						11	10	9122.4652	0.0001
						9	8	9122.4707	0.0011
10	1	9	9	1	8	9	8	9244.9358	-0.0011
						11	10	9244.9428	0.0007
						10	9	9245.0205	0.0000
10	2	8	9	2	7	10	9	9359.3813	-0.0001
						11	10	9359.4077	-0.0012
						9	8	9359.4123	-0.0002
11	1	11	10	1	10	12	11	9251.4311	0.0007
						10	9	9251.4413	-0.0003
						11	10	9251.4670	-0.0005
11	0	11	10	0	10	12	11	9329.3892	-0.0002
						10	9	9329.3967	0.0004
						11	10	9329.4632	0.0003
11	2	10	10	2	9	12	11	9763.9166	-0.0001
						10	9	9763.9200	0.0005
						11	10	9763.9672	0.0004
11	3	9	10	3	8	12	11	9950.5021	-0.0003
						10	9	9950.5021	-0.0019
						11	10	9950.5316	-0.0009
11	4	8	10	4	7	12	11	9954.9607	-0.0014
						10	9	9954.9607	-0.0006
						11	10	9955.0034	0.0004
11	3	8	10	3	7	11	10	10072.1982	0.0005
						12	11	10072.2232	0.0000
						10	9	10072.2288	0.0004
11	1	10	10	1	9	10	9	10112.9832	-0.0005
						12	11	10112.9890	0.0001
						11	10	10113.0764	-0.0002
11	2	9	10	2	8	11	10	10320.1384	-0.0009
						12	11	10320.1537	-0.0005
						10	9	10320.1558	-0.0002
12	1	12	11	1	11	13	12	10071.3519	-0.0005
						11	10	10071.3615	-0.0005
						12	11	10071.3862	-0.0008
12	0	12	11	0	11	13	12	10130.3350	-0.0002
						11	10	10130.3426	0.0006
						12	11	10130.3974	0.0005
12	2	11	11	2	10	11	10	10624.1796	-0.0015
						13	12	10624.1796	0.0008
						12	11	10624.2285	0.0008
12	3	10	11	3	9	13	12	10853.8096	-0.0009
						11	10	10853.8121	0.0001
						12	11	10853.8365	-0.0010
12	1	11	11	1	10	11	10	10963.4878	-0.0005
						13	12	10963.4931	0.0001
						12	11	10963.5887	-0.0005
12	3	9	11	3	8	12	11	11033.9799	0.0014

Table S25. Continued.

$J^{'}$	$K^{'}_{-1}$	$K^{'}_{+1}$	$J^{''}$	$K^{''}_{-1}$	$K^{''}_{+1}$	$F^{'}$	$F^{''}$	Obs.	Obs. - Calc
12	3	9	11	3	8	13	12	11034.0171	0.0003
						11	10	11034.0235	0.0012
13	1	13	12	1	12	14	13	10888.8559	-0.0002
						12	11	10888.8648	0.0004
						13	12	10888.8882	0.0000
13	0	13	12	0	12	14	13	10932.3699	-0.0008
						12	11	10932.3773	0.0001
						13	12	10932.4215	-0.0006
13	2	12	12	2	11	14	13	11478.3609	0.0003
						12	11	11478.3638	0.0011
						13	12	11478.4107	0.0018

Table S26. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{18}O_{w1}$ isotologue of the complex *cis*-fa-w_2-a in the ground vibrational state.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
7	0	7	6	0	6	8	7	6017.6862	-0.0010
						6	5	6017.6978	0.0011
						7	6	6017.8023	0.0007
8	0	8	7	0	7	9	8	6822.3376	-0.0016
						7	6	6822.3471	-0.0013
						8	7	6822.4474	-0.0017
9	1	9	8	1	8	10	9	7502.1654	-0.0002
						8	7	7502.1821	-0.0001
						9	8	7502.2031	-0.0059
9	0	9	8	0	8	10	9	7618.1270	-0.0016
						8	7	7618.1449	0.0089
						9	8	7618.2280	0.0011
9	2	8	8	2	7	8	7	7930.7332	-0.0045
						10	9	7930.7332	-0.0012
						9	8	7930.7908	-0.0011
9	3	7	8	3	6	8	7	8048.7923	0.0007
						10	9	8048.7923	0.0004
						9	8	8048.8400	-0.0008
9	3	6	8	3	5	8	7	8100.7483	-0.0019
						10	9	8100.7483	0.0010
						9	8	8100.7652	0.0062
9	1	8	8	1	7	8	7	8264.7780	-0.0028
						10	9	8264.7855	-0.0009
						9	8	8264.8617	0.0019
9	2	7	8	2	6	9	8	8314.7210	-0.0001
						10	9	8314.7580	0.0021
						8	7	8314.7580	-0.0031
10	1	10	9	1	9	11	10	8316.5441	-0.0001
						9	8	8316.5593	0.0016
						10	9	8316.5829	-0.0017
12	0	12	11	0	11	13	12	9988.6770	-0.0005
						11	10	9988.6853	0.0007
						12	11	9988.7391	0.0017

Table S27. Observed rotational transitions with resolved ^{14}N hyperfine structure and residuals (all the values in MHz) for the $^{18}O_{w2}$ isotologue of the complex *cis*-fa-w_2-a in the ground vibrational state.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	Obs.	Obs. - Calc
7	0	7	6	0	6	8	7	5925.5262	-0.0019
						6	5	5925.5381	0.0001
						7	6	5925.6360	-0.0004
8	0	8	7	0	7	9	8	6723.1304	-0.0006
						7	6	6723.1406	0.0006
						8	7	6723.2377	0.0000
9	1	9	8	1	8	10	9	7384.8021	-0.0008
						8	7	7384.8193	-0.0003
						9	8	7384.8435	-0.0009
9	0	9	8	0	8	10	9	7511.2266	-0.0006
						8	7	7511.2345	0.0011
						9	8	7511.3261	0.0009
9	2	8	8	2	7	10	9	7782.5339	-0.0001
						8	7	7782.5339	-0.0036
						9	8	7782.5877	-0.0005
9	3	7	8	3	6	8	7	7881.9117	0.0000
						10	9	7881.9117	0.0000
						9	8	7881.9596	-0.0004
9	3	6	8	3	5	8	7	7920.2319	-0.0004
						10	9	7920.2319	0.0020
						9	8	7920.2500	0.0019
9	1	8	8	1	7	8	7	8103.1118	-0.0014
						10	9	8103.1193	0.0010
						9	8	8103.1822	-0.0002
9	2	7	8	2	6	9	8	8113.1067	0.0004
						10	9	8113.1440	-0.0008
						8	7	8113.1525	0.0013
10	1	10	9	1	9	11	10	8188.5280	-0.0025
						9	8	8188.5421	-0.0019
						10	9	8188.5659	-0.0035
12	0	12	11	0	11	13	12	9851.3609	0.0007
						11	10	9851.3684	0.0019
						12	11	9851.4247	0.0007
13	1	13	12	1	12	14	13	10582.1370	0.0005
						12	11	10582.1475	0.0028
						13	12	10582.1694	0.0011