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Crystal and Molecular Structure of a Nickel(II) Compound Derived from 2-Methylpropane-1,2-diamine: $[Ni(C_{18}H_{21}N_4)]ClO_4$

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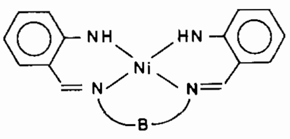
Crystals of the title compound are monoclinic, a = 19.25(4), b = 13.91(1), c = 14.66(3) Å, β = 94.56(2)°, space group $B2_1/a$. *A three dimensional X-ray analysis of the structure was made with counter data (2244 independent reflections). The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares to R 0.058. The monocation contains an* $[NiN_4]$ *four co-planar polyhedron with Ni–N distances of 1.848(6) Å (anionic amido), 1.875(6) and 1.880(5) Å (azomethine) and 1.928(6) Å (primary amine). The ligand is an unusual Schiff base combination of a dimer of 2-aminobenzaldehyde with a terminal diamine. The* ^1H *n.m.r. spectra of the salts of this cation are discussed in the light of this structure, and 'covalent hydration' is suggested as an explanation of the observed differences in aqueous solution.*

Introduction

During our study [1] of the compounds I, we isolated a novel product from one attempt to prepare



I

the compound I for B = $\cdot CH_2\cdot CMe_2\cdot$. This had the empirical formula $Ni(C_{18}H_{21}N_4)X$ (where X = OAc, or ClO_4).

An X-ray analysis of one of the two crystalline forms of the perchlorate (the β-form) was undertaken to determine the nature of the cation. A preliminary report has already appeared [2] and here we present the final details of the analysis.

Experimental

Dark red plates were obtained from ethanol. The data crystal had dimensions 0.16 X 0.26 X 0.17 mm. Cell dimensions were determined by a least-squares analysis of the ω-dependence of 25 reflections.

Crystal Data

$C_{18}H_{21}N_4NiClO_4$, M = 451.6, Monoclinic, a = 19.25(4), b = 13.91(1), c = 14.66(3) Å, β = 94.56(2)°, U = 3913 Å^3, D_m (flotation) = 1.51 g cm^{-3}, Z = 8, D_c = 1.53 g cm^{-3}, $F(000)$ = 1872. Space group $B2_1/a$ {a non-standard setting of $P2_1/c$ [C^5_{2h}, No. 14], chosen for the convenient β angle}. MoKα radiation, λ = 0.7107 Å, μ(MoKα) = 11.63 cm^{-1}.

X-ray data, with 6.5° < 2θ < 50° for layers $h0l \rightarrow h18l$, were collected from a crystal mounted up the b axis on a Stoë Stadi-2 diffractometer in the stationary-counter–moving-crystal mode, using graphite-monochromated MoKα radiation.

Angular step-scan ranges for the reflections were systematically varied to allow for variations in peak-width. A counting time of 1.0 s was used for each 0.01° increment of scan. Background counts were accumulated for 30 s at each extremity of the scan.

Reflections with intensity I < 3σ(I) were ignored, as were those with background differences $\Delta > 3\sigma_B$. Lorentz and polarisation corrections were applied. At a late stage in the refinement absorption corrections were calculated and applied. However, as they led to no improvement in the R factor, they were then discarded. The complete data set comprised 2244 reflections.

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TABLE 1. Atomic Positions and Thermal Vibrational Parameters. Estimated standard deviations are given in parentheses.

(a) Atomic positions ($\times 10^4$) of non-hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*
Ni	730.1(4)	2804.2(6)	64.7(5)
Cl	944(1)	−571(2)	−1345(1)
O(1)	1112(5)	106(6)	−650(6)
O(2)	1445(6)	−528(9)	−1975(7)
O(3)	932(5)	−1505(5)	−1012(6)
O(4)	291(5)	−372(7)	−1789(8)
N(1)	122(3)	1831(4)	−494(4)
N(2)	185(3)	3656(4)	−680(4)
N(3)	1315(3)	3772(4)	589(3)
N(4)	1140(3)	1862(4)	816(4)
C(1)	−293(3)	2201(6)	−1331(4)
C(2)	167(6)	2189(6)	−2132(5)
C(3)	−958(4)	1586(7)	−1539(6)
C(4)	−470(4)	3223(6)	−1063(5)
C(5)	326(4)	4528(5)	−885(4)
C(6)	969(4)	5015(5)	−576(4)
C(7)	1119(4)	5891(5)	−993(5)
C(8)	1732(5)	6359(6)	−803(5)
C(9)	2226(4)	5965(6)	−166(5)
C(10)	2089(4)	5111(5)	276(5)
C(11)	1451(4)	4632(5)	102(4)
C(12)	1643(3)	3701(5)	1426(4)
C(13)	1728(3)	2866(5)	1951(4)
C(14)	2084(4)	2935(6)	2842(5)
C(15)	2227(4)	2138(6)	3372(5)
C(16)	2039(4)	1226(6)	3009(5)
C(17)	1708(4)	1117(6)	2163(5)
C(18)	1510(3)	1947(5)	1609(4)

(b) Hydrogen atom positions[a] ($\times 10^3$)

N(N1)	40	130	−66	5.68
H(N1a)	−19	161	−6	5.68
H(4)	−81	322	−62	6.08
H(4a)	−66	358	−158	6.08
H(5)	−2	488	−126	5.22
H(7)	78	616	−144	6.07
H(8)	182	694	−111	6.37
H(9)	266	629	−3	6.29
H(10)	243	484	72	5.58
H(12)	184	428	169	5.12
H(14)	222	357	307	5.92
H(15)	247	220	397	6.03
H(16)	214	66	337	5.86
H(17)	158	49	193	5.79
H(N4)	107	121	60	5.47

(c) Anisotropic thermal parameters[b] ($\times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni	182(0)	378(1)	260(0)	−62(1)	−12(1)	−38(1)
Cl	384(1)	486(2)	506(2)	−35(5)	15(2)	−108(2)
O(1)	692(6)	953(9)	1095(10)	−1108(16)	−444(12)	279(12)

(continued on facing page)

TABLE I. *(continued)*

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O(2)	1082(9)	1835(16)	1054(10)	−592(22)	1158(16)	−1380(21)
O(3)	963(7)	678(8)	925(9)	440(13)	424(13)	283(12)
O(4)	628(6)	1114(12)	2007(17)	−393(22)	−877(17)	378(14)
N(1)	255(3)	468(5)	365(5)	−19(8)	17(6)	−186(6)
N(2)	200(3)	488(5)	313(4)	−149(8)	−20(5)	50(6)
N(3)	202(2)	363(4)	232(4)	−13(7)	7(5)	−4(5)
N(4)	278(3)	415(5)	335(4)	−111(7)	−50(6)	−6(6)
C(1)	185(3)	527(6)	305(4)	−131(10)	5(6)	−19(8)
C(2)	273(3)	598(7)	382(5)	−308(12)	134(7)	−70(10)
C(3)	225(4)	836(10)	541(7)	−284(14)	−176(8)	−335(10)
C(4)	209(3)	621(7)	445(6)	−303(11)	35(7)	66(8)
C(5)	255(3)	471(6)	280(5)	−53(9)	−30(7)	159(8)
C(6)	249(3)	389(5)	248(4)	−64(8)	−10(6)	83(7)
C(7)	401(5)	440(6)	338(6)	83(10)	170(8)	132(9)
C(8)	416(5)	478(7)	434(6)	102(11)	318(9)	−62(9)
C(9)	356(4)	537(7)	394(6)	−41(11)	172(8)	−113(9)
C(10)	260(3)	441(6)	342(5)	50(9)	54(7)	−137(8)
C(11)	247(3)	323(5)	292(5)	−55(8)	55(6)	24(7)
C(12)	218(3)	431(6)	287(5)	−38(9)	28(6)	−45(7)
C(13)	195(3)	403(5)	242(4)	119(9)	17(5)	−49(7)
C(14)	236(3)	609(8)	388(6)	−19(11)	−70(7)	46(9)
C(15)	273(3)	715(8)	334(5)	198(12)	−76(7)	54(10)
C(16)	278(4)	558(7)	364(5)	274(10)	92(7)	50(9)
C(17)	281(4)	474(7)	469(6)	217(10)	−44(8)	−24(8)
C(18)	200(3)	404(6)	289(5)	66(8)	5(6)	−46(6)

[a] Except for those especially noted, hydrogen atoms take the same number as the carbons to which they are attached. [b] The expression for the temperature factor is exp $[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

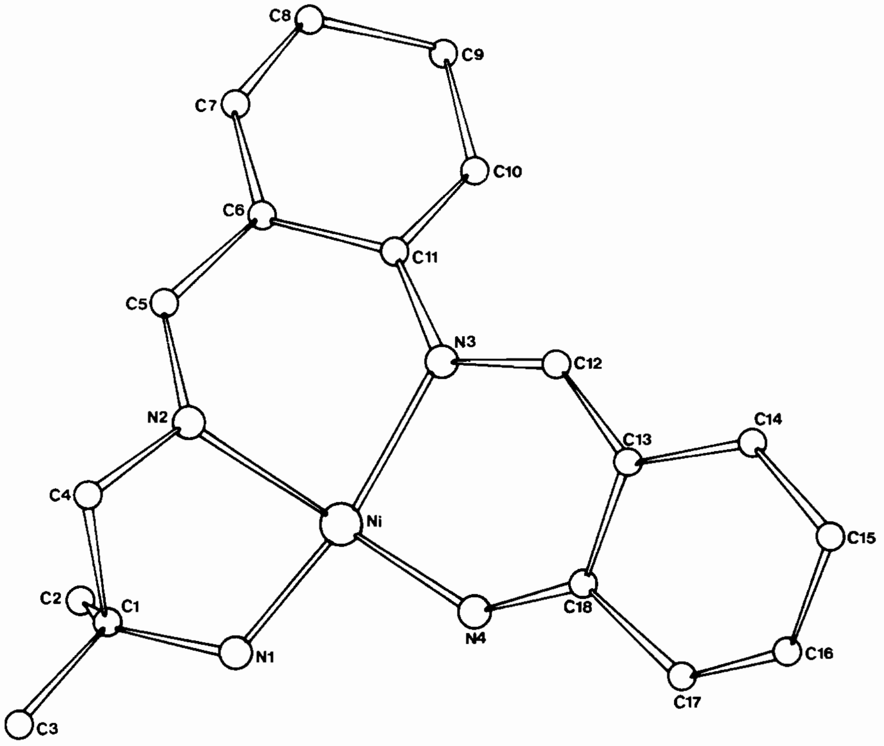


Fig. 1. The molecular cation and the atom labelling scheme.

TABLE II. Interatomic Distances (Å) and Angles (°). Estimated standard deviations are in parentheses.

Bond Lengths (Å)		Bond Angles (°)			
Ni–N(1)	1.928(6)	N(1)–Ni–N(2)	84.5(2)		
Ni–N(2)	1.875(6)	N(2)–Ni–N(3)	94.3(2)		
Ni–N(3)	1.880(5)	N(3)–Ni–N(4)	93.0(2)		
Ni–N(4)	1.848(6)	N(1)–Ni–N(4)	88.3(2)		
N(1)–C(1)	1.501(9)	Ni–N(1)–C(1)	111.9(4)		
C(1)–C(2)	1.526(10)	N(1)–C(1)–C(2)	108.8(6)	C(2)–C(1)–C(3)	111.3(6)
C(1)–C(3)	1.550(11)	N(1)–C(1)–C(3)	110.5(6)	C(2)–C(1)–C(4)	111.5(6)
C(1)–C(4)	1.521(10)	N(1)–C(1)–C(4)	103.0(5)	C(3)–C(1)–C(4)	111.6(6)
C(4)–N(2)	1.468(9)	C(1)–C(4)–N(2)	106.1(6)		
N(2)–C(5)	1.283(9)	Ni–N(2)–C(4)	112.8(4)	C(4)–N(2)–C(5)	119.3(6)
		Ni–N(2)–C(5)	127.9(5)		
C(5)–C(6)	1.452(9)	N(2)–C(5)–C(6)	124.0(6)	C(5)–C(6)–C(11)	122.7(6)
		C(5)–C(6)–C(7)	118.0(6)		
C(6)–C(7)	1.403(10)	C(7)–C(6)–C(11)	119.3(6)		
C(7)–C(8)	1.357(11)	C(6)–C(7)–C(8)	122.3(7)		
C(8)–C(9)	1.391(11)	C(7)–C(8)–C(9)	119.0(8)		
C(9)–C(10)	1.388(11)	C(8)–C(9)–C(10)	120.4(7)		
C(10)–C(11)	1.403(10)	C(9)–C(10)–C(11)	121.2(7)		
C(11)–C(6)	1.409(9)	C(10–C(11)–C(6)	117.8(6)		
C(11)–N(3)	1.427(8)	N(3)–C(11)–C(6)	122.2(6)	Ni–N(3)–C(11)	121.6(4)
		N(3)–C(11)–C(10)	120.0(6)	Ni–N(3)–C(12)	123.0(4)
				C(11)–N(3)–C(12)	115.4(5)
N(3)–C(12)	1.339(8)	N(3)–C(12)–C(13)	126.4(6)		
		C(12)–C(13)–C(14)	118.3(6)	C(12)–C(13)–C(18)	122.3(6)
C(13)–C(14)	1.429(10)	C(18)–C(13)–C(14)	119.3(6)		
C(14)–C(15)	1.369(11)	C(13)–C(14)–C(15)	121.6(7)		
C(15)–C(16)	1.411(11)	C(14)–C(15)–C(16)	118.7(7)		
C(16)–C(17)	1.357(11)	C(15)–C(16)–C(17)	122.2(7)		
C(17)–C(18)	1.445(10)	C(16)–C(17)–C(18)	120.6(7)		
C(18)–C(13)	1.424(9)	C(17)–C(18)–C(13)	117.5(6)		
C(18)–N(4)	1.320(9)	C(13)–C(18)–N(4)	121.0(6)	C(18)–N(4)–Ni	129.5(5)
		C(17)–C(18)–N(4)	121.6(6)		
Cl–O(1)	1.406(9)	O(1)–Cl–O(2)	108.7(6)	O(2)–Cl–O(4)	109.2(7)
Cl–O(2)	1.390(12)	O(1)–Cl–O(3)	112.4(5)	O(3)–Cl–O(4)	108.1(6)
Cl–O(3)	1.388(9)	O(1)–Cl–O(4)	110.6(6)		
Cl–O(4)	1.396(11)	O(2)–Cl–O(3)	107.8(6)		
The H-bonds					
O(1)–N(1)	3.08(1)	N(1)–H(N1)•••O(1)	164		
O(1)–H(N1)	2.15				
O(1)–N(4)	3.25(1)	N(4)–H(N4)•••O(1)	147		
O(1)–H(N4)	2.40				
O(3′)–N(1)	3.15(1)[a]	N(1)–H(N1a)•••O(3′)	166[a]		
O(3′)–H(N1a)	2.22[a]				

[a] The primted atom is at –x, –y, –z.

The structure was solved by conventional Patterson and Fourier techniques, and refinement, using block-diagonal least-squares methods, proceeded smoothly to a final R of 0.058.

Anisotropic thermal parameters were used for all non-hydrogen atoms; a non-unit weighting was used in which $w = 1$ for $|F_o| < 20.0$ and $\sqrt{w} = 20.0/|F_o|$ for $|F_o| > 20.0$; anomalous dispersion corrections (both $\Delta f'$ and $\Delta f''$) were applied to the atomic scattering factors for all non-hydrogen atoms [3].

Hydrogen atoms (except for those attached to the methyl carbons) were observed in a difference Fourier and thus were included, but not varied, at calculated positions (0.96 Å) for the final refinement. Isotropic thermal parameters 2.0 larger than those for the appropriate carbon or nitrogen were assigned to these hydrogen atoms.

TABLE III. Equations to Least-Squares Planes. These are given in the form $lX + mY + nZ = d$ (where X, Y and Z are coordinates in Å referred to the axes a, b and c^*). Deviations (Å) of the various atoms from these planes are given in square brackets.

	l	*m*	*n*	*d*
Plane (1):	N(1), N(2), N(3), N(4)			
	−0.6966	0.1505	0.7015	−0.2800
	[Ni −0.04, N(1) −0.05, N(2) 0.04, N(3) −0.04, N(4) 0.04, C(1) −0.34, C(2) −1.84, C(3) −0.98, C(4) 0.41, C(5) −0.19, C(6) −0.61, C(7) −1.09, C(8) −1.60, C(9) −1.64, C(10) −1.15, C(11) −0.58, C(12) 0.43, C(13) 0.72, C(14) 1.24, C(15) 1.47, C(16) 1.13, C(17) 0.61, C(18) 0.44].			
Plane (2):	N(2), N(3), C(5), C(6), C(11)			
	−0.5847	0.4462	0.6776	1.4187
	[Ni −0.43, N(2) −0.08, N(3) 0.07, C(4) −0.01, C(5) 0.09, C(6) −0.01, C(7) −0.07, C(10) −0.31, C(11) −0.07, C(12) 0.54]			
Plane (3):	N(3), N(4), C(12), C(13), C(18)			
	0.8981	−0.1614	−0.4090	1.0036
	[Ni −0.42, N(3) 0.01, N(4) −0.02, C(11) 0.39, C(12) 0.00, C(13) −0.03, C(14) −0.06, C(17) 0.18, C(18) 0.04]			
Plane (4):	Ni, N(1), N(2)			
	0.6780	−0.1160	−0.7258	0.4267
	[C(1) 0.35, C(2) 1.87, C(3) 0.65, C(4) −0.35, C(5) 0.27]			
Plane (5):	C(6)–C(11)			
	−0.4627	0.5152	0.7214	2.1161
	[C(6) −0.02, C(7) 0.01, C(8) 0.01, C(9) −0.01, C(10) – 0.01, C(11) 0.02, N(2) −0.41, N(3) 0.07, C(5) −0.14]			
Plane (6):	C(13)–C(18)			
	−0.9117	0.0786	0.4032	−1.3491
	[C(13) −0.01, C(14) −0.01, C(15) 0.02, C(16) −0.00, C(17) −0.02, C(18) 0.03, N(3) −0.14, N(4) 0.12, C(12) −0.14]			

Angles (°) between planes:

(1)–(2)	18.2	(1)–(6)	21.6	(2)–(5)	8.4
(1)–(3)	159.5	(2)–(3)	151.0	(3)–(6)	175.2
(1)–(5)	25.1	(5)–(6)	41.1		

The final difference Fourier had a highest peak of 0.24 $e\text{Å}^{-3}$.

Observed structure amplitudes and the calculated structure factors are in a Table available from the Editor.

Programmes used for the refinement were part of the Sheffield X-ray System.

Final atomic positional and vibrational parameters are listed in Table I, and the atom-labelling scheme is given in Fig. 1.

Results and Discussion

The molecular cation shown by the analysis (Fig. 1) is a four-coplanar nickel(II) polyhedron with the ligand being a novel monoanionic condensation product – rather than the dimeric structure we originally proposed [1].

Bond lengths and angles are given in Table II, and some least-squares planes for the cation are in Table III.

The Ni–N bond lengths reflect the different nitrogen donors: Ni to anionic amido N {N(4)} is shortest at 1.848(6) Å; Ni to azomethine N's {N(2) and N(3)} average 1.878(6) Å; and Ni to primary amine N {N(1)} is longest at 1.928(6) Å. All are within the range observed for other low-spin planar nickel(II) species [4]. Angles within the [NiN_4] polyhedron are defined by the sizes of the chelate rings; and there is only a small tetrahedral distortion of this plane (Table III – nitrogens are ±0.04 Å from least-squares plane), resulting from the ligand conformation.

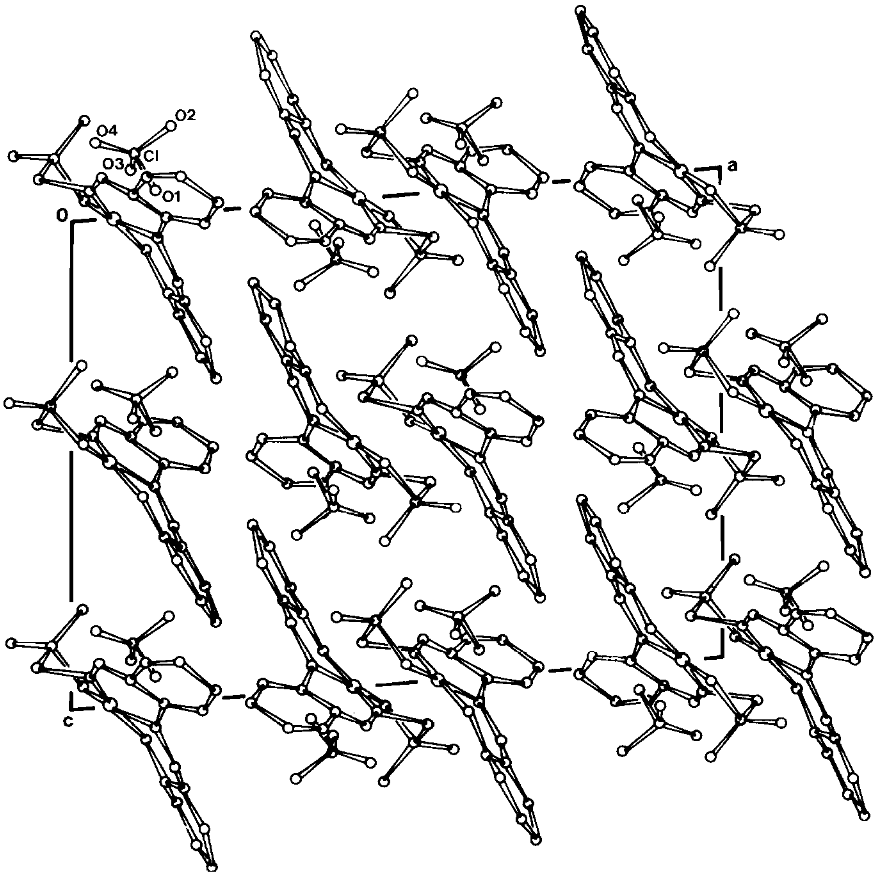


Fig. 2. The packing of the ion pairs in the crystal: a projection down the *b* axis.

The whole molecule is far from planar (Table III); the *o*-iminobenzaldimine chelate rings are inclined at 29 °C to each other, and form dihedral angles of +18 and –20 °C with the [NiN_4] plane (Table III).

Some strain in the ligand system is indicated by the non-planarity of N(2) with the phenylene group to which it is attached (0.41 Å, Table III). Otherwise, bond lengths and angles with the chelate system are unexceptionable, as they are in the perchlorate.

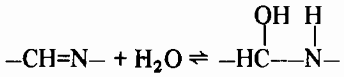
The latter is H-bonded, both inter- and intramolecularly, by relatively weak H-bonds ($N\cdots O = 3.08 \rightarrow 3.25$ Å, see Table II). O(1) is bound both to the primary amine and to the amido group of the same molecule. The ion-pairs and the way in which they pack in the crystal are shown in Fig. 2.

In our paper describing these compounds [1], we noted that the ^1H n.m.r. spectrum of the perchlorate in DMSO, and that of the acetate in $CDCl_3$, differed markedly from that of the acetate in D_2O. The most significant differences are in the positions of the azomethine protons: in DMSO the two different protons (Fig. 1) resonate in much the same position near 8.65 p.p.m.; whereas in aqueous solution, they are moved upfield, and one much further than the other (7.91 p.p.m. for the one, and the other is mixed in with other aromatic proton resonances between 7.6 and 6.6 p.p.m.).

It is clear from the present structure determination that such differences between solvents cannot arise from conformations of the molecule: there is only one; and neither does ion-pairing offer an explanation. Rather it seems that 'covalent hydration' (addition of water to the azomethines) must be the cause.

The closeness of the resonances for the apparently two different azomethines in DMSO and $CDCl_3$ is a result of the conformation of the molecule. The azomethine lying between the two phenylenes is not affected by the second phenylene because it lies in just that region where there is a neutral crossover between shielding and de-shielding effects from this aromatic ring.

The differences then with the aqueous solution (the upfield shifts and wider separation of the resonances) must result from the interaction of water with the azomethines, and probably in the form of a 'covalent hydrate' equilibrium:



$$-CH{=}N- + H_2O \rightleftharpoons -\overset{OH}{\overset{|}{HC}}-\overset{H}{\overset{|}{N}}-$$

This would also explain the observation [1] that different DMSO solutions showed small differences in the separation between signals: different small amounts of water in the hygroscopic DMSO lead to different amounts of the 'covalent hydrate'. One solution made up from a fresh ampoule of DMSO gave a separation of only 0.02 p.p.m. for the azomethine signals, but other solutions showed separations of up to 0.06 p.p.m.

The formation of this unsymmetrical mono-cation in one, but not other, of our reactions mixtures [1] was probably the result of a kinetic effect: significant self-condensation of the *o*-aminobenzaldehyde, followed by termination of this by the diamine, and 'trapping' of the resultant ligand by the nickel.

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