

Proton Magnetic Resonance of Some Schiff Bases of Acetylacetonone and Diamines and of their Nickel(II) Complexes

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The proton magnetic resonance of chelated and free Schiff bases of unsymmetric diamines (such as 1,2-propanediamine) and two molecules of acetylacetonone has been studied. The two acetylacetonone parts are magnetically inequivalent in the examined compounds, and this fact is interpreted both for the free Schiff bases and their nickel complexes.

The ¹H-NMR-spectra of Schiff bases of β-diketones with diamines, and metal complexes of such ligands, have already been investigated by several authors. Dudek and Holm¹ showed that the ligands should properly be formulated as ketoenamines. McCarthy and Martell² compared the ¹H-NMR-spectra of series of these ligands with those of the corresponding diamagnetic nickel(II), palladium(II), and platinum(II) complexes. They also reported results for Schiff base derivatives of some unsymmetric diamines. For these compounds, it was observed that the two vinyl hydrogens on the acetylacetonone skeletons (H_α, H_β in Fig. 1) were magnetically different. The origin

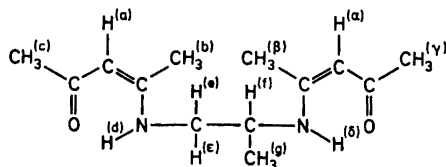


Fig. 1.

and magnitude of this inequality remained unexplained. The present paper extends the NMR-studies of such Schiff bases, as well as their nickel(II) complexes, in order to discuss these problems. A rather detailed knowledge of

the geometric arrangement has emerged from this study, and will be compared with the existing information, based upon electronic spectra and circular dichroism.^{3,4}

EXPERIMENTAL

Analytical data for the compounds used, and reference to the preparations, are given in Table 1. Two of the Schiff bases reported here appear to have been prepared for the first time.

Table 1. Analytical data for the compounds used.

	Ref.	Calc.			Found		
		C	H	N	C	H	N
pn(acacH) ₂	5	65.5	9.23	11.75	65.82	9.38	11.93
Ni pn(acac) ₂	5	53.0	6.78	9.50	53.10	6.89	9.37
1,3-bn(acacH) ₂		66.6	9.52	11.11	66.88	9.62	11.20
phenen(acacH) ₂		71.97	8.05	9.33	71.85	8.03	9.30
Ni phenen(acac) ₂		60.56	6.17	7.85	60.50	6.17	7.88

phenen(acacH)₂. 1-Phenyl-1,2-ethanediamine was prepared from phenylglyoxime by reduction with sodium in methanol.⁶ The Schiff base was made from 5 ml of the amine and 8 ml of freshly distilled acetylacetone. The mixture was heated to 60°C for 1 h with 30 ml of benzene. After drying the solution with Al₂O₃, crystallization was induced by adding petrol ether. Recrystallization from benzene. M.p. 81–82°.

Ni phenen(acac)₂ was prepared, following a procedure similar to that used for Ni pn(acac)₂.⁵

1,3-bn(acacH)₂. 1,3-Butanediamine was prepared by condensing acetonitrile to β-iminobutyronitrile and reducing this compound with sodium in methanol.⁷ 1,3-bn(acacH)₂ was prepared in the same way as the above Schiff base. M.p. 67–68°.

The compounds were dissolved in analytical grade solvents, and TMS was added as an internal standard. The concentrations were 5–10 %.

NMR-spectra were recorded on Varian A 60 and HA 100 spectrometers at 32°C, unless otherwise specified. Spectra at 100 MHz were obtained in frequency sweep mode, using a sweep modification described earlier.⁸

The homonuclear INDOR experiment⁹ was performed, using two external oscillators. A Hewlett-Packard oscillator 4201 A was introduced as sweep oscillator in J 1308 on the back of the lock box. The frequency was adjusted to the center of the desired signal.

A Wavetek 111 VCO oscillator was used as variable frequency external oscillator. The frequency was linked to the motion of the recorder pen.⁸

Line positions have been measured relative to TMS with an accuracy of ±0.1 Hz.

DISCUSSIONS

McCarthy and Martell² have previously measured the ¹H-NMR of Ni pn(acac)₂. Our results (see Table 2) are in agreement with theirs, but the resolution obtained here is somewhat better; it should, therefore, be possible to give a more detailed assignment of the observed peaks. However, the structures of the bands are complicated, and it has been necessary to turn to the INDOR technique.⁹ Fig. 2 shows the total spectrum of Ni pn(acac)₂, and the NMR-signals from the CH₂CH fragment of the diamine are shown in Fig. 3. The high field doublet with a spacing of 12.2 Hz is assigned to one of the methylene

Table 2. Chemical shifts and coupling constants for the compounds in CDCl_3 solutions. The $^1\text{H-NMR}$ signals have been identified as stated in the text. The relative order of the signals α, α , b, β , and c, γ has no significance.

	Chemical shifts (ppm)								Coupling constants (Hz)					
	α, α	b, β	c, γ	e	e	f	g	$d-e, e$	$\delta-f$	$e-e$	$f-e$	$f-e$	$f-g$	
$\text{Ni pn}(\text{acac})_2$	4.851, 4.893	1.835, 1.861	1.871, 1.883	3.143	2.633	3.268	1.311	—	—	-12.7	5.6	~1	6.2	
$\text{Ni phenen}(\text{acac})_2$	4.829, 4.931	1.636, 1.720	1.872, 1.923	3.55	2.97	4.22	$\begin{cases} 7.44^a (o) \\ 8.18^a (m, p) \end{cases}$	—	—	-12.8	6.4	~0.0	—	
$\text{pn}(\text{acacH})_2$	4.966, 4.992	1.928, 1.957	2.046	3.290	2.290	3.714	1.250	6.5	9.8	—	6.5	6.5	6.5	
$\text{phenen}(\text{acacH})_2$	4.960, 5.035	1.803, 1.821	1.985, 2.060	3.554	3.554	4.670	7.32 ^a	6.7	9.0	—	6.75	6.75	—	
$1,3\text{-bn}(\text{acacH})_2^b$	4.939, 4.964													

^a The signals from the phenyl protons are given for these two compounds.

^b The bridge between the conjugated parts contains two methylene groups.

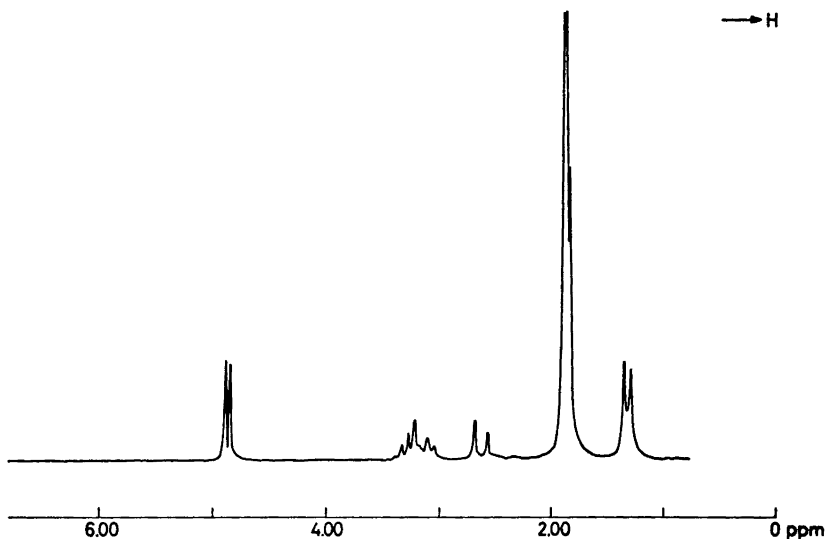


Fig. 2. $^1\text{H-NMR}$ spectrum of $\text{Ni pn}(\text{acac})_2$ in CDCl_3 .

protons, since this separation is characteristic of a *geminal* coupling constant. The low field multiplet represents the other methylene proton and the neighbouring CH proton. In a homonuclear INDOR experiment, where the sample is irradiated with the frequency of one of the doublet lines, the spectrum B in Fig. 3 is obtained. Changing the radiation frequency to that of the other doublet line yields the spectrum C. The *gem* coupling constant of 12.7 Hz, and a *vic* coupling constant of 5.6 Hz were obtained from the four lines in the spectra B and C. The absence of further splitting of the high field doublet indicates that the $\text{H}_e - \text{H}_f$ coupling constant is *small* (between 0 and 1). The spectrum has been parameterized, as given in Table 2, by means of the computer programme LAOCOON(II).¹⁰

There is a large difference in chemical shifts between H_e and H_f . In $\text{Ni en}(\text{acac})_2$, however, all four methylene protons have the same chemical shift, which is consistent with a rapid interchange between two symmetric conformations in this complex. Introduction of a methyl (or phenyl, *vide infra*) group creates a large energy separation between the two conformers, and accordingly $\text{Ni pn}(\text{acac})_2$ behaves as if fixed in one conformation. Assumption of the qualitative validity of Karplus' equation¹¹ leads to dihedral angles for $\text{H}_e - \text{H}_f$ and $\text{H}_e - \text{H}_g$ of some 30° and 90° , respectively.

This arrangement is only possible with the methyl group (with H_g) being an axial substituent in the Ni-NCCN -ring with a conformation about the bridging C-C bond, as shown in Fig. 4. It has been inferred from absorption and circular dichroism spectra that this complex has an almost planar arrangement of the nickel atom and the four ligating atoms.⁴ If the two conjugated parts of the ligand were co-planar, we would expect the effective symmetry of the molecule to be D_{2h} . However, the doubling of all the signals from the

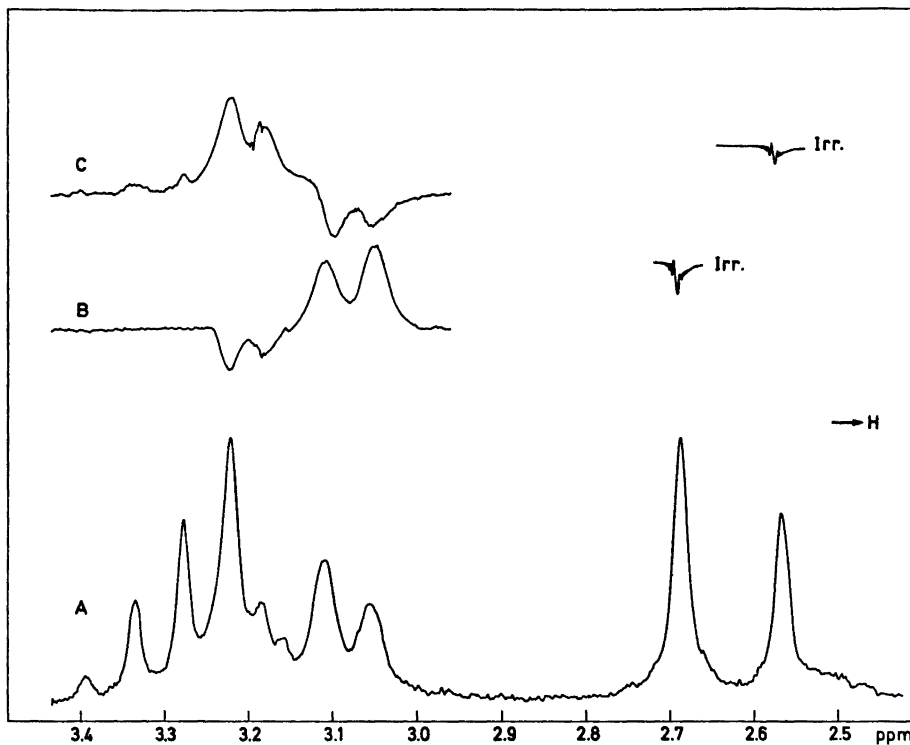


Fig. 3. Detail from the 100 MHz ^1H -NMR spectrum of Ni pn(acac) $_2$ in the range 2.5–3.4 ppm. A, the normal spectrum. B, INDOR irradiating at low field line in the doublet. C, INDOR irradiating at high field line in the doublet.

a,α , b,β , and c,γ protons show that the methyl group on the bridge introduces a significant difference between the two halves. With the restriction of the system made by the geometric arrangement of the bridge and by the near planarity of the ligands we conclude that the acetylacetonate part, marked with Greek letters in Fig. 1, must be bent out of the coordination plane to minimize the repulsion between H_α and H_β .

The NMR-spectrum of Ni phenen(acac) $_2$ has been interpreted in the same way as that of Ni pn(acac) $_2$, and with qualitatively the same results for the

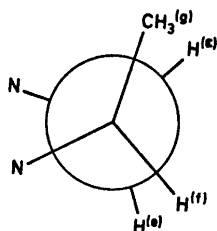


Fig. 4. Newman projection along the bridging C–C bond in Ni pn(acac) $_2$, in accordance with the coupling constants given in Table 2.

geometry, but the greater separation in the chemical shifts of the α, α protons suggests a more pronounced distortion, out of the coordination plane, for one acetylacetonate moiety. The resultant chemical shifts and coupling constants are given in Table 2.

It is noteworthy that, while the phenyl protons in the free ligand yield only a single resonance signal, there is a large difference between the chemical shifts of the *ortho* protons and the *meta*, *para* protons in the nickel complex. The signal of the *o*-protons in the complex is shifted by approx. 70 Hz to low field, compared to the situation for the free ligand; the other phenyl protons are not shifted significantly. Molecular models clearly show that the *o*-hydrogen atoms are much closer to the nickel atoms than the *m*- and *p*-protons.

The $^1\text{H-NMR}$ -spectrum of the free ligand $\text{pn}(\text{acac})_2$ is similar, in certain regions, to that of the nickel complex. The signals due to the H_e , H_g , and H_i atoms were simplified to a doublet and a sextet, with an integral ratio of 2:1 by deuterating the nearby d, δ hydrogens. The coupling constant $J_{i,g}$ was found to be 6.5 Hz from the splitting in the signal from the *g*-proton. H_i gives rise to the sextet, since only this signal is affected by decoupling with the frequency of the signal due to H_g . Both $J_{e,i}$ and $J_{g,i}$ have the same value, measured as the splitting of the doublet. This explains the integral ratios of the components in the sextet, which are 1:5:10:10:5:1. The protons H_e and H_g have the same chemical shifts and the same coupling constants to H_i . This means that the bridge between the acetylacetonate parts is rather flexible. However, the pronounced differences in the chemical shifts between the α, α , the β, β , and the γ, γ protons proves that there is not a free rotation about the bridging C-C bond. Solution UV and CD spectra have led to the conclusion that the two conjugated parts are close to each other and not in an anti conformation.³ The combined information, then, gives a picture of a molecule in which the two conjugated parts are attracted towards each other by electric dipole-dipole forces, the negative pole of one of the two parts always being near the positive pole of the other acetylacetonate part. This explains the chemically different surroundings for the two conjugated moieties. The 1,2-propylene fragment, which functions as the bridge, has a large degree of vibrational and rotational freedom. This interpretation seems to the present authors to be more satisfactory than that² in terms of a large magnetic anisotropy arising from the methyl group on the bridge. This anisotropy should be larger on the distant H_α , H_α than on the near H_β , H_β , in order to explain the observations.

Further evidence for the interpretation given here can be found in the NMR-spectra of 1,3-bn(acacH)₂. For this molecule, one would expect even more flexibility in the bridge between the acetylacetonate units than in $\text{pn}(\text{acacH})_2$. However, the two conjugated parts are also inequivalent in this molecule (see Table 2). Again, the findings can be interpreted by the model postulated above for $\text{pn}(\text{acacH})_2$.

The relative stabilities of the two "intramolecular molecular complexes" in $\text{pn}(\text{acacH})_2$ and 1,3-bn(acacH)₂ have been judged by studying the variation with temperature of the signals due to H_α and H_α . In CDBr_3 solutions, the NMR signals for $\text{pn}(\text{acacH})_2$ remained unchanged until ca. 120°C, when an irreversible change in the spectrum was observed. For 1,3-bn(acacH)₂, how-

ever, it was observed that the signals for H_a and H_α collapsed at 70°C; the effect was reversible. This reflects the higher degree of flexibility present in 1,3-bn(acacH)₂ as compared to pn(acacH)₂.

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