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The Solution Structure of the Bis-(1,5-diazacyclooctane)nickel(II) Ion: an NMR Study

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Abstract

The 300 MHz proton NMR spectrum of bis-(1,5-diazacyclooctane)nickel(II) [Ni(DACO)$_2$$^{2+}$] perchlorate in D_2O has been analysed. The vicinal coupling constants indicate that the C_3N_2Ni six-membered chelate rings exist as rapidly-inverting chair and boat conformations, rather than the completely planar C_3N_2Ni chelate rings suggested by an earlier crystal structure. The spectrum shows no significant change at low temperature (down to *ca.* −90 °C), indicating a low barrier for the ring inversion process.

Introduction

X-ray crystallography has traditionally been the method of choice for the experimental determination of the structures of metal complexes. However, among its disadvantages are: (i) it requires the availability of suitable crystals; (ii) certain types of crystal disorder may lead to incorrect structures [1]; and (iii) it offers no insight into the dynamics of conformational interconversions like those recently reported for the nickel(II) complex of 1,4,8,11-tetraazacyclotetradecane [2]. NMR spectroscopy, on the other hand, avoids these difficulties, and thus serves as an ideal complement to crystallographic studies.

We have undertaken a systematic investigation of the applicability of modern 1D- and 2D-NMR methods to the study of the structures and dynamics of nickel(II) complexes [3]. As part of this work we sought simple complexes which had been characterized crystallographically, and were intrigued by the report that the six-membered C_3N_2Ni chelate rings of bis-(1,5-diazacyclooctane)nickel(II) perchlorate are planar [4]. The accumulation of torsional strain thereby suggested seemed unusual, even considering the apparently highly crowded nature of the system. Our suspicions were strengthened when numerous attempts to refine its structure by molecular mechanics calculations** using the published structure as a starting point led to structures with chair and/or boat chelate rings, as found by Boeyens *et al.* [6], of whose work we were unaware at the time. However, in our hands, the molecular mechanics calculations led variously to two conformations, one with four chair rings (the 'lobster claw') and the other with two chair and two boat rings (the 'pinwheel'), whose energies were too close to allow us to choose between them. Accordingly, we analysed its 300 MHz proton NMR spectrum to ascertain whether the vicinal couplings would support such a novel conformation. Our results indicate that the structure cannot be correct, but rather that the structure is a dynamic one, with the six-membered chelate rings apparently inverting rapidly between chair and boat conformations, thereby confirming and extending the recent work of Boeyens *et al.* [6], who reinterpreted the published X-ray data with the aid of molecular mechanics calculations.

Experimental

Spectra were obtained on a Varian XL-300 NMR spectrometer operating at a frequency of 299.943 MHz and equipped with a 5 mm multinuclear probe. We employed a 5 μs (20°) pulse and an acquisition time of 2.3 s. The spectral widths were approximately 1.8 KHz and the size of the transform was variously 8 or 16 K. The water resonance was reduced by application of a saturating pulse. Chemical shifts were referenced to the methyl peak of t-butyl alcohol (δ 1.20), a small amount of which was added as an internal standard. Line positions used in the spectral simulations were taken from resolution-enhanced spectra. Sample concentration was approximately 7–8 mg of $Ni(DACO)_2(ClO_4)_2$ per ml of D_2O. Spectra showed no change even after the samples had stood for over a month.

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**We used the program MODEL, from the laboratory of Clark Still (Columbia University), with parameters for square-planar nickel taken from the literature [5]. The calculations were done on a VAX 11/780 computer.

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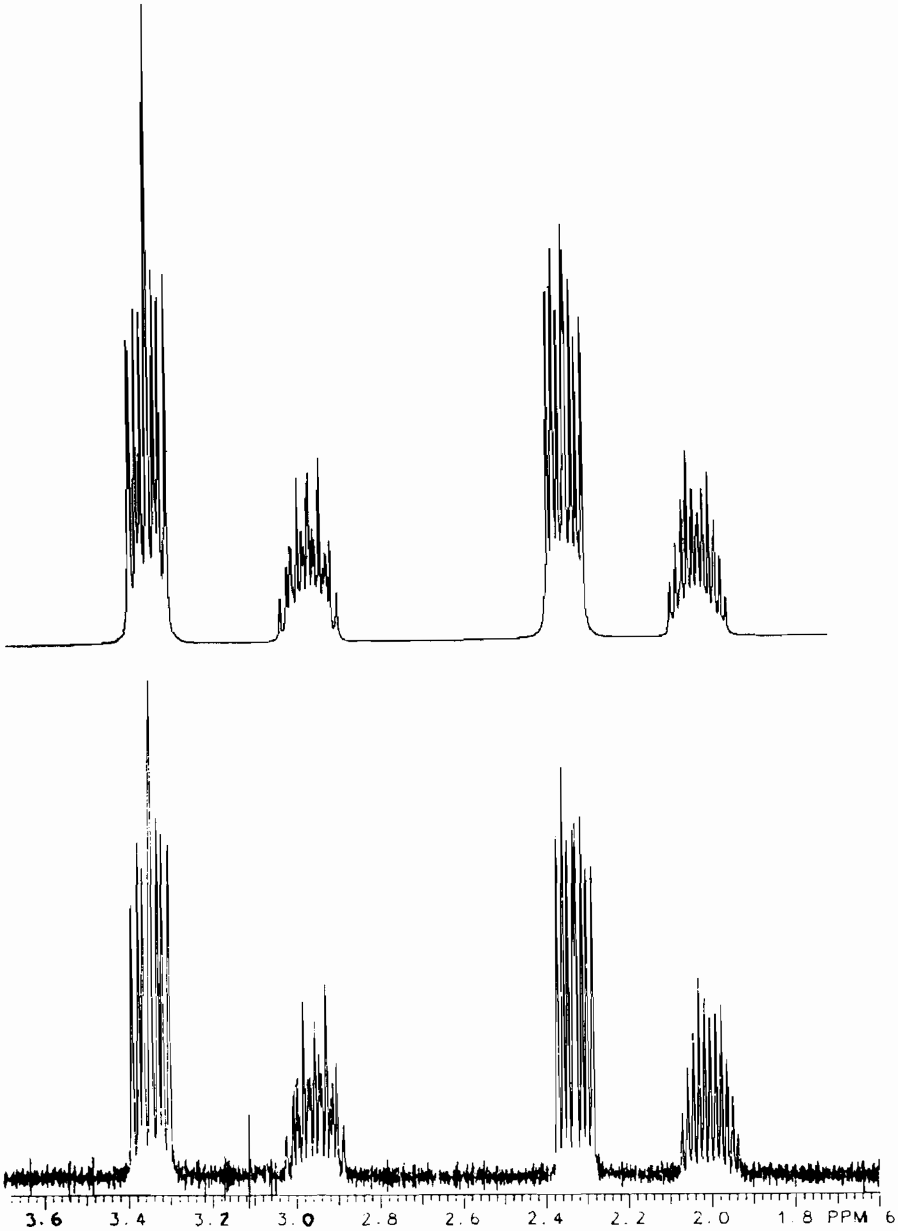

Fig. 1. 300 MHz proton NMR spectrum of $Ni(DACO)_2^{2+}$ in D_2O. Lower trace: resolution-enhanced experimental spectrum. Upper trace: spectrum calculated with parameters given in Table I and a linewidth of 2 Hz.

TABLE I. Proton NMR Spectral Parameters for $Ni(DACO)_2^{2+}$

	A[a, b]	B	C	C′	D	D′
A	δ1.980	−15.75	4.01	4.01	8.34	8.34
B		δ2.931	7.84	7.84	4.87	4.87
C			δ2.304	0.00	−13.46	0.00
C′				δ2.304	0.00	13.46
D					δ3.321	0.00
D′						δ3.321

[a] Since the chemical shifts are dynamically averaged, no attempt was made to differentiate the pairs A/B, C/D or C′/D′. [b] Probable errors are <0.001 ppm for chemical shifts and <0.05 Hz for coupling constants.

Results and Discussion

The 300 MHz proton spectrum of Ni(DACO)$_2^{2+}$ in D$_2$O (Fig. 1) is reasonably well-resolved and of ABCC′DD′ symmetry. The spectrum was simplified by several decoupling experiments which allowed extraction of approximate vicinal and geminal coupling constants, which were then used as the starting point for an iterative computer fit of the full spectrum using the program LAOCN-5 [7]*. A total of 107 out of 160 transitions were assigned, and the r.m.s. error between calculated and observed transitions was 0.207 Hz. The resulting parameters are summarized in Table I**. The ABCC′DD′ system is characterized by four vicinal coupling constants, $J_{AC} = J_{AC'}$ (4.0 Hz), $J_{AD} = J_{AD'}$ (7.8 Hz), $J_{BC} = J_{BC'}$ (8.4 Hz), and $J_{BD} = J_{BD'}$ (4.9 Hz), whose magnitudes are inconsistent with static structures for the six-membered chelate rings. In the conformationally-locked Ni(II)–1,4,7,10-tetraazacyclotridecane complex, where the six-membered ring is in the chair form, the anti vicinal coupling is 13 Hz, while the three gauche couplings are all approximately 3 Hz [3]. While the extended Karplus equation [9] has not yet been parameterized to predict vicinal couplings in systems such as these, it seems reasonable to expect an approximately cos^2 dependence of J_{vic} on torsion angle, so that a planar ring should exhibit two large syn (0°, $J = 13$ Hz) and two small (120°, $J = 3$ Hz) couplings. The observed couplings seem inconsistent with either such a structure†, or a static structure with four equivalent chair or boat conformations. A static structure with alternating chair and boat rings as found by Boeyens *et al.* [6] (the 'pinwheel' conformation) can be ruled out due to the simplicity of the spectrum, which indicates only one type of ring. However, the data are consistent with a structure like that found by Boeyens *et al.* [6], provided rapid inversion of the chelate rings is occurring. Inspection of Dreiding models of the 'pinwheel' conformation of Ni(DACO)$_2^{2+}$ suggests that the trimethylene fragments of both chair and boat conformations should exhibit three gauche and one anti vicinal couplings. Ring inversion interchanges the 13 Hz anti coupling of the chair conformation with the 3 Hz gauche coupling of the boat form, giving a dynamically-averaged coupling of about 8 Hz. Similarly, the 13 Hz anti coupling in the boat conformation becomes a 3 Hz gauche coupling in the chair form, giving a second 8 Hz averaged coupling. Two gauche couplings remain unaffected, accounting for the set of coupling constants derived from the NMR spectrum. Interestingly, the crystal disorder reported by Boeyens shows two conformationally-equivalent 'pinwheel' structures related by four ring inversions, consistent with either a 1:1 mixture of static conformations or a dynamic situation in which conformational interconversion is slow on the X-ray time scale. Extrapolation of our results for the ion in aqueous solution to the structure in the solid state must be done with considerable caution; nonetheless, the latter possibility seems more attractive.

We attempted to observe the chair-boat ring inversions directly in low-temperature spectra, using methanol-d$_4$ as solvent§. However, even at −80 °C, no significant spectral changes were observed, other than minor line broadening, indicating the inversion barrier to be a low one.

References

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*Chen *et al.* [8] report gauche couplings of about 3 Hz and anti couplings of about 13 Hz for a series of tetraaza macrocycle Ni(II) complexes.

**The simulated decoupled spectra also agreed well with experiment, though iterative fits were not done.

†Assuming that some unprecedented electronic effect is not operative here.

§Spectra of Ni(DACO)$_2^{2+}$ in D$_2$O and in CD$_3$OD were essentially identical.