

Conformational Characterization of a Nickel(II) Tetraazamacrocyclic Complex through Isotropic Shift Studies of the Dinuclear Cobalt(II)–Nickel(II) Derivative

LUCIA BANCI and ANDREA DEI

Istituto di Chimica Generale ed Inorganica dell'Università di Firenze, Laboratorio C.N.R., Via Jacopo Nardi 39, 50132 Florence (Italy)

Received February 26, 1979

Recently it has been shown [1] that ^1H NMR spectra of both homo- and hetero-dinuclear paramagnetic metal complexes formed by the ligand 2-pyridyl methyl ketazine (PMK) can be interpreted on the basis of a simple model. The isotropic shift $\Delta H_i/H$ (MM') experienced by a ligand proton i in a given $\text{MM}'(\text{PMK})_3^{4+}$ complex can be considered as given by the sum of two contributions, one from the metal M which is closer to the given resonating proton, the other from the metal M' which is farther, according to the relationship

$$\frac{\Delta H_i}{H} (\text{MM}') = \frac{\Delta H_i}{H} (M) + \frac{\Delta H_i'}{H} (M')$$

This simple additive model (which recalls the supertransferred hyperfine field model suggested by Kokoszka [2] in order to justify the esr spectra of copper(II) dimers) can be assumed to be valid as long as the exchange interactions between the two metal ions are small.

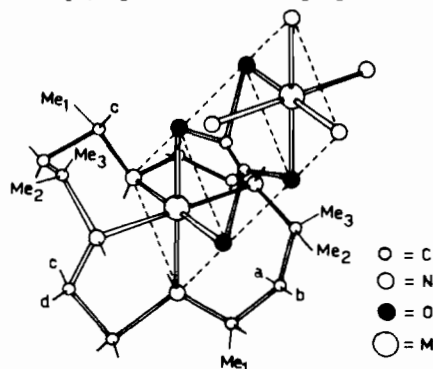
Further, it was shown that when heterodinuclear species are considered, the presence of a paramagnetic metal ion characterized by a very short electronic relaxation time can reduce significantly the line width of the signals of protons closer to a different paramagnetic metal ion characterized by a longer electronic relaxation time.

Both these effects were suggested to be important in order to characterize through ^1H NMR spectroscopy stable or labile paramagnetic dinuclear metal complexes containing either the same and different metal ions. Here we report some new results which further support this conclusion.

It is well known that isotropic shift studies can provide a powerful tool for obtaining conformational information, since it has been shown that the contact shift contribution depends on the conformational character, *i.e.* axial or equatorial, of the resonating proton [3–5]. The application of this technique, however, is often limited by the broadness of the signals, which makes difficult the detection and the

assignment of non-equivalent proton sets. As to the last point, although we succeeded in the conformational characterization of *trans*-octahedral tetraazamacrocyclic nickel(II) complexes through isotropic shift studies [5], we have found serious difficulties in interpreting the ^1H NMR spectra of solutions containing *cis*-octahedral nickel(II) complexes formed by the same ligands. For instance, the nickel(II) complexes of general formula $[\text{NiLX}]Y$ formed by the ligand *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($\text{Me}_6[14]\text{aneN}_4$) ($X = \text{HCOO}$, CH_3COO , NO_3 , *acac*; $Y = \text{ClO}_4$, PF_6) can be postulated to contain NiLX^+ cations, the macrocyclic ligand being folded and coordinated to four adjacent octahedral sites of the metal ion [6, 7]. The conformation of the ligand in these complexes, as ascertained by an X-ray diffraction analysis on the $[\text{Ni}(\text{Me}_6[14]\text{aneN}_4)(\text{CH}_3\text{COO})]\text{ClO}_4$ derivative [6], is such that the six- and five-membered chelate rings are in a chair and gauche conformation, respectively, so that in the idealized C_2 symmetry there are ten sets of nonequivalent protons. However the ^1H NMR spectra of the solutions of these complexes do not provide information because of the large line width of the signals of the resonating protons.

We have therefore considered the compound $[\text{Ni}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$, which on the basis of ir data and magnetic properties has been postulated to contain oxalato-bridged dimeric cations [7, 8]. We have also prepared the cobalt(II)



analogue, which on the basis of the similarity of the ir spectra and conductometric behavior (see Experimental), appears to contain similar dimeric cations.

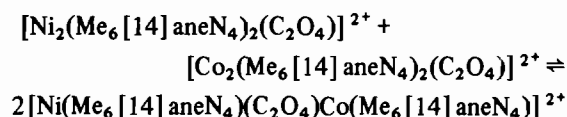
The ^1H NMR spectral data at 34 °C for d_6 -DMSO solutions of the two complexes are reported in Table I. The ^1H NMR traces of the same solutions in the approximate range $-30/+20$ ppm with respect to Me_4Si are shown in Fig. 1. The spectrum of the nickel(II) derivative is very similar to those of the monomeric nickel(II) complexes; the spectrum of the cobalt(II) compound shows a well resolved pattern of resonances characterized by smaller line widths, as a result of the shorter electronic spin–lattice relax-

TABLE I. Isotropic Shift Data (ppm)^a and Spectral Assignments for [MM'(Me₆[14]aneN₄)₂(C₂O₄)]²⁺ Complexes in d₆-DMSO at 34 °C. ^{b,c}

Complex	Me _{eq} (Me ₁ , Me ₂) ^c	Me _{ax} (Me ₃) ^c	β-CH _{ax} (a) ^c	β-CH _{eq} (b) ^c	α-CH _{ax} (c) ^c	α-CH _{eq} (d) ^c
[Ni ₂ (Me ₆ [14]aneN ₄) ₂ (C ₂ O ₄)] ²⁺	-10.8 (-11.7, -9.6)	2.9 (2.3) ^f	d (7) ^e (7.4) ^f	15.7 (15.6) ^f	d	d
[Co ₂ (Me ₆ [14]aneN ₄) ₂ (C ₂ O ₄)] ²⁺	-16.1, 7.1 (-16.3, 7.0) ^f	83.8 (83.2) ^f	74.5	58.9 (58.8) ^f	-36, 4.2	g
[CoNi(Me ₆ [14]aneN ₄) ₂ (C ₂ O ₄)] ²⁺	Co	68.5	72.1	55.0	(-43) ^h	g
	Ni	-8.9, -6.8	17.6	9.8	19.5	(-29) ^h

^aThe isotropic shifts are determined relative to the shifts of the free ligand: α-CH -2.8 (average), β-CH -1.7 (average), Me -1.1 (average). Estimated errors in isotropic shift data: 1 ppm. ^bKey: ax = axial; eq = equatorial. ^cSee Fig. 1. ^dNot detected because of its broadness. ^eExpected value (see ref. 5). ^fCalculated by the sum of the corresponding ΔH'/H(M) values in the heterodinuclear species and the difference between the corresponding ΔH'/H(M') values in the heterodinuclear and M'-homodinuclear species. ^gNot detected probably because of the large value of the isotropic shift. ^hTentatively assigned. Other resonances not detected because of the overlap with other signals.

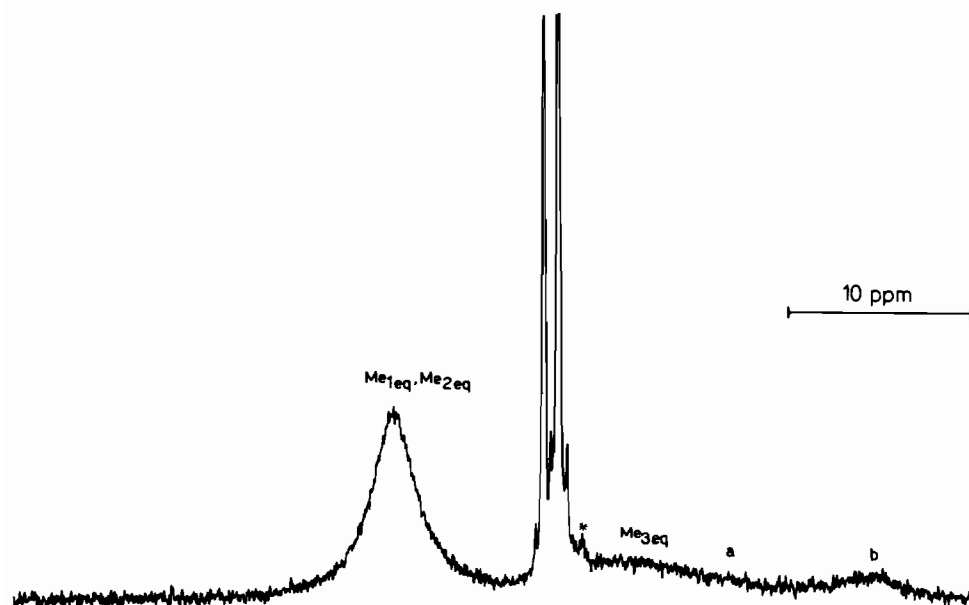
ation time of high-spin octahedral cobalt(II) as compared to that of octahedral nickel(II). Furthermore if the solutions containing the two complexes are mixed together, the spectrum of the resulting solution (spectrum c) shows other signals, which do not correspond to those observed for the two pure dinuclear complexes. It is apparent that an heterodinuclear species is formed, according to the equilibrium



As observed for PMK complexes [1], the prominent feature of the heterodinuclear species is the neat decrease of the line width of the protons closer to the nickel(II) ion as compared to those observed in the homodinuclear derivative: in particular this sharpening allowed us to observe all the expected signals of the macrocyclic ligand bound to the nickel(II) ion.

The assignment of the resonances has been performed on the basis of the following considerations:

- (i) the intensity ratios;
- (ii) in absence of dipolar contributions, the ethylenic protons and the α-propylenic protons are



(a) Fig. 1. (continued on facing page)

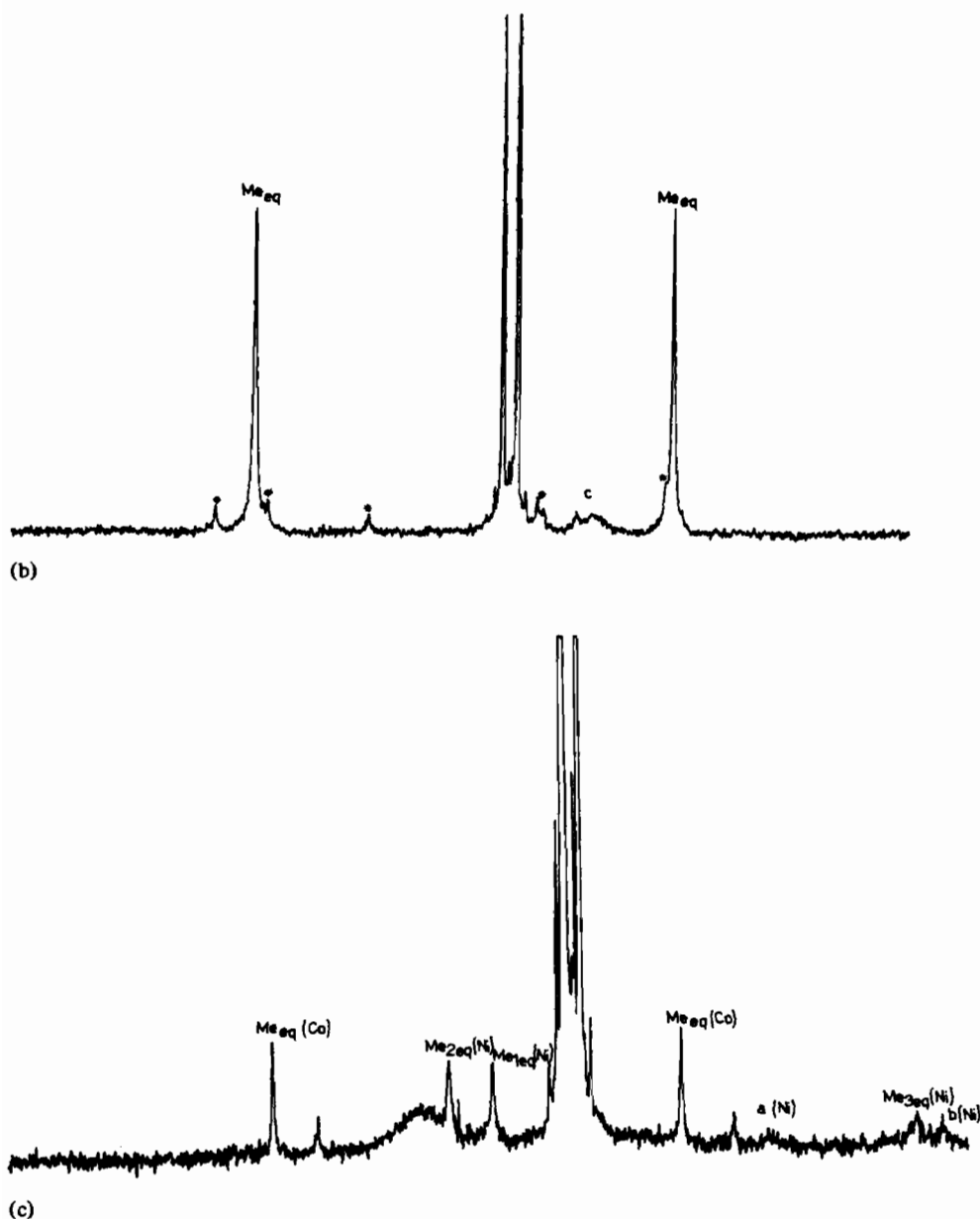


Fig. 1. Proton magnetic resonance spectra (range: $-30/+20$ ppm with respect to tetramethylsilane reference) of d_6 -DMSO solutions of (a) $[\text{Ni}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$, (b) $[\text{Co}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$ (signals labeled with * are due to isomeric impurities) and (c) $\text{CoNi}(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$. Intense signals are due to the solvent. In the last spectrum the unlabeled signals are due to homodinuclear species.

- expected to experience downfield shifts, as referenced to the diamagnetic positions, whereas β -methylene protons of the propylene chain are expected to shift upfield, because of spin polarization mechanisms [4, 9];
- (iii) the axial proton resonances are expected to be broader than those of the equatorial protons, since the former protons are closer to the paramagnetic metal ion and therefore more affected by a dipolar relaxation mechanism [10].

The assignment of the resonances of the methyl groups of the nickel(II) derivative is supported by the spectra of a sample containing selectively deuterated geminal methyl groups.

In addition to these considerations, which have been successfully used in determining the conformational properties of nickel(II) complexes [3–5], the previously outlined additive model provides an useful method in order to obtain a correct assignment of most resonance signals.

The direct application of the model is here possible, since exchange interactions in these dimeric complexes are expected to be small. Magnetic susceptibility experiments indicate the existence of a weak antiferromagnetic interaction ($J = -18 \text{ cm}^{-1}$) in the $[\text{Ni}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2$ complex [8]. For the cobalt(II) derivative no data are available; however it should be suggested that the exchange interaction between two cobalt(II) ions should be weaker than for the nickel(II) complex [11]. Following the procedure outlined in Table I, we calculate, when possible, isotropic shift values which correspond quite closely to those observed, assuming that the contribution $\Delta H'/H(M')$ due to the nickel(II) is negligible. The reliability of this hypothesis is supported by the fact that the spectrum of the homodinuclear nickel(II) derivative is very similar to those of the mononuclear ones.

It is worth noting that the postulated conformation of the macrocyclic ligand clearly shows up from the observed pattern of resonances, when compared with the spectra of other macrocyclic complexes [5]. The observed number of signals supports the postulated symmetrical arrangement of the macrocyclic ligand around the two metal ions; for the nickel(II) derivative the signals of the axial and equatorial ethylenic geminal protons are well split, thus indicating the existence of a regular gauche conformation of the ethylenic chains, and the different conformational character of the methyl groups is accounted for by the different sign of the hyperfine coupling constant.

The results reported here show how the formation of an appropriate heterodinuclear species can be used to elucidate the conformational structure of paramagnetic complexes formed by metal ions characterized by unfavourable electronic relaxation times. This in principle can be very important when isotropic shift studies are necessary for characterizing a paramagnetic species.

Experimental

The racemic isomer of the ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ($\text{Me}_6[14]\text{aneN}_4$) was prepared according to Tait and Busch [12].

Cobalt(II) and nickel(II) μ -oxalato dinitrate derivatives of general formula $[\text{M}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$ were prepared using the following procedure. To a methanolic solution of the appropriate $\text{M}(\text{Me}_6[14]\text{aneN}_4)(\text{NO}_3)_2$ was added a methanolic solution containing the required stoichio-

metric amounts of oxalic acid and triethylamine. The resulting solution was concentrated under nitrogen until crystallization occurred. The complex was filtered, washed with methanol and ether and dried *in vacuo*. *Anal.* $\text{C}_{34}\text{H}_{72}\text{N}_{10}\text{O}_{10}\text{Co}_2$ requires: C, 45.42; H, 8.07; N, 15.58; Found: C, 45.3; H, 7.9; N, 15.4. $\text{C}_{34}\text{H}_{72}\text{N}_{10}\text{O}_{10}\text{Ni}_2$ requires: C, 45.45; H, 8.07; N, 15.58; Found: C, 45.5; H, 8.0; N, 15.7.

Physical Properties

$[\text{Co}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$: $\mu = 4.66$ (295 K); $\Lambda_{(\text{DMSO})}^{20^\circ} = 73 \text{ mho cm}^2$. Absorption max (kK) (ϵ_{molar} in parentheses): 9.4 (21.4), 20.6 (58.7).

$[\text{Ni}_2(\text{Me}_6[14]\text{aneN}_4)_2(\text{C}_2\text{O}_4)](\text{NO}_3)_2$: $\mu = 2.99$ BM (295 K), $\Lambda_{(\text{DMSO})}^{20^\circ} = 69 \text{ mho cm}^2$. Absorption max (kK) (ϵ_{molar} in parentheses): 10.3 (37), 17.2 (40.5), 26.3 (63.6).

^1H NMR Measurements

Proton magnetic resonance spectra were recorded on a Varian EM 390 spectrometer at 90 MHz. Shifts were calibrated from internal tetramethylsilane. Hexadeuteriodimethylsulphoxide (Merck 99.5%) was used as solvent.

Acknowledgments

We thank Professor L. Sacconi for constant encouragement. We are indebted to Mr. G. C. Vignozzi for microanalyses and to Mr. F. Cecconi for magnetic measurements.

References

- 1 A. Dei, D. Gatteschi and E. Piergentili, *Inorg. Chem.*, **18**, 89 (1979).
- 2 G. F. Kokoszka and R. W. Duerst, *Coord. Chem. Rev.*, **5**, 209 (1970).
- 3 R. H. Holm and C. J. Hawkins, 'NMR of Paramagnetic Molecules', Academic Press, New York (1973) p. 243.
- 4 J. E. Sarneski and C. N. Reilley, *Inorg. Chem.*, **13**, 977 (1974).
- 5 A. Dei, *Inorg. Chem.*, **18**, 000 (1979).
- 6 P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. A*, 1956 (1970).
- 7 N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1968).
- 8 D. M. Duggan, E. K. Barefield and D. N. Hendrickson, *Inorg. Chem.*, **12**, 985 (1973).
- 9 M. J. Scarlett, A. T. Casey and R. A. Craig, *Aust. J. Chem.*, **23**, 1333 (1970).
- 10 D. R. Eaton and W. D. Phillips, *Adv. Magn. Res.*, **1**, 103 (1965).
- 11 P. W. Ball and A. B. Blake, *J. Chem. Soc. Dalton Trans.*, 852 (1974).
- 12 A. M. Tait and D. H. Busch, *Inorg. Nucl. Chem. Lett.*, 491 (1972).