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A PMR Investigation of the Paramagnetic tris(bipyridine-N,N'-dioxide)Nickel(II) and Cobalt(II) Complexes

I. Bertini, D. Gatteschi, and L.J. Wilson

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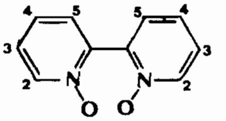
Pmr spectra of the tris(bipyridine-N,N'-dioxide)nickel(II) and cobalt(II) cations [$Ni(bipyO_2)_3^{2+}$ and $Co(bipyO_2)_3^{2+}$] are reported and the isotropic shifts are attributed to a dominating π delocalization mechanism onto the aromatic phenyl rings. The ratio method[1] has been used to factor the cobalt isotropic shifts into their contact and dipolar components and, concurrently, to obtain detailed structural information about the ligand conformation in solution. The angle between the two tipped phenyl rings of the chelated $bipyO_2$ molecule has been determined to be 67°.

Introduction

It is well known that bipyridine-N,N'-dioxide ($bipyO_2$) acts as a bidentate ligand in forming pseudooctahedral metal complexes with nickel(II) and cobalt(II).[2] Chelation through the oxygen donor atoms results in a seven membered chelate ring which forces the two phenyl rings to be tipped relative to one another. The resulting nonplanarity of the two chelate rings may give rise to both *d* and *l* ligand diastereoisomers which, when combined with the Δ and Λ possibilities for tris pseudooctahedral complexes, results in a total of eight possible optical isomers.[3] Four of these isomers could, in principle, be detected by pmr[4] *i.e.* $\Delta ddd \equiv \Lambda lll$ $\Delta lll \equiv \Lambda ddd$, $\Delta ddl \equiv \Lambda lld$, $\Delta dll \equiv \Lambda lld$, $\Delta dll \equiv \Lambda ldd$. If the spin delocalization mechanism in the $bipyO_2$ ligand is the same for both the nickel and cobalt complexes, as is known to be the case for pyridine-N-oxide complexes,[5] it is possible to factor the cobalt isotropic shifts into their dipolar and contact components using the so-called ratio method,[1] and subsequently obtain detailed information concerning the nature of the ligand conformation in solution.



Bipyridine-N,N'-dioxide

Results

Despite the isomers possibilities,[6] only four pmr resonances have been detected for each complex, as shown in Figure 1. Two of the signals are upfield and two are downfield from internal TMS. The upfield peaks are assigned to the 2–H and 4–H protons by analogy with the reported resonance positions of nickel(II) and cobalt(II) pyridine-N-oxide complexes[5] and by the usual signal width consideration *i.e.* the 2–H proton gives rise to the broadest signal due to its nearest to the paramagnetic center.[7] The downfield resonances which are attributed to the 3–H and 5–H protons cannot be assigned on the basis of simple considerations, however equation 1 calculations (see discussion section) have permitted the reasonable proton assignment shown in Figure 1. The isotropic shifts for both complexes are reported in Table I.

Discussion

Origin of the peaks. The alternating up- and downfield proton pattern as displayed by the $Ni(bipyO_2)_3^{2+}$ species is clearly indicative of π spin delocalization onto the aromatic rings.[7,8] The close vicinity of the 2–H and 4–H signals excludes the possibility of significant dipolar shift contributions arising from magnetic anisotropy, as is the usual case for pseudooctahedral nickel(II) complexes.[1,9] For the $Co(bipyO_2)_3^{2+}$ complex, the 2–H proton resonance shows a marked upfield shift as compared to the 4–H proton signal position. Furthermore, the 3–H and 5–H resonances are separated by 12.5 ppm whereas a separation of only 0.92 ppm is found for the nickel(II) complex. These significant differences between the nickel and cobalt spectra undoubtedly arise from strong

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(1) W. De W. Horrocks, jr., *Inorg. Chem.*, *9*, 690 (1970).
(2) P. G. Simpson, A. Vinciguerra, and J. V. Quagliano, *Inorg. Chem.*, *2*, 282 (1963).
(3) A. D. Liehr, Transition Metal Chemistry, 2, 165 (1966).
(4) R. H. Holm, *Accounts of Chem. Res.*, *2*, 307 (1969), and references therein.
(5) R. W. Kluiber and W. De W. Horrocks, jr., *J. Am. Chem. Soc.*, *87*, 5350 (1965)
(6) Y. T. Chen, and G. W. Everett, jr., *J. Am. Chem. Soc.*, *90*, 6660 (1968).
(7) D. R. Eaton and W. D. Phillips, Advan. Magnetic Resonance, *1*, 103 (1965).
(8) I. Bertini, D. L. Johnston, and W De W. Horrocks, jr., *Inorg. Chem.*, *9*, 698 (1970).
(9) M. L. Wicholas and R. S. Drago, *J. Am. Chem. Soc.*, *90*, 2196 (1968).

Table I. Isotropic, Contact, and Dipolar shifts for the Nickel(II) and Cobalt(II) BipyO$_2$ Complexes[a, b]

Proton position	$G_i(\text{Å}^{-3})$ [c]	$\Delta\nu_{Ni}^{isotropic}(i)$	$\Delta\nu_{Co}^{isotropic}(i)$	$\Delta\nu_{Co}^{contact}(i)$	$\Delta\nu_{Co}^{dipolar}(i)$	$\frac{\Delta\nu^{contact}(i)}{\Delta\nu^{contact}(4)}$ Ni	Co
2	0.020775	36.4	77.9	46.8	31.1	0.995	1.063
3	0.002595	−13.4	−12.3	−16.2	3.88	−0.366	−0.368
4	−0.006907	36.6	40.1	44.0	−3.87	1.000	1.000
5	−0.002581	−12.5	−24.8	−14.5	−10.3	−0.341	−0.329

[a] In ppm at 26°C in d$_3$-acetonitrile from internal tetramethylsilane (TMS). [b] Isotropic shifts determined relative to the reported chemical shifts of pyridine-N-oxide:[5] 2-H, −8.20 ppm; 3,4-H, −7.27 ppm from TMS. [c] Geometrical factors calculated using a M—O distance of 2.20 Å and a O—M—O angle of 85°.

dipolar shift interactions which are well known to be operative in pseudo octahedral cobalt(II) complexes.[10,11]

For each position, the *ddl* or *lld* isomer would theoretically give rise to two pmr resonances (with intensities 2:1) whose separation should be especially enhanced by differing dipolar shifts contributions in the case of the cobalt(II) species.[10,12] As shown in Figure 1, no such multiplicity is experimentally observed. Although a rapid chelate ring $d \rightleftharpoons l$ interconversion or rapid ligand exchange process could account for the observed peak singlets, both processes seem unlikely- the first, because of the anticipated high barrier to chelated ligand interconversion and the second, because no fast ligand exchange was found to occur in a solution containing both « free » (bipyO$_2$) and « complexed » (M(bipyO$_2$)$_3^{2+}$) ligand. Since no peak multiplicity is observed between −40°C and +30°C, it seems reasonable to conclude that the only isomers present in appreciable amounts are the $\Delta ddd (\equiv \Lambda lll)$ and the $\Delta lll (\equiv \Lambda ddd)$, whose signals are degenerate within the limits of the instrument resolution and peak broadness.

Solution structural information. Assuming that the mechanisms of spin delocalization onto the bipyO$_2$ ligand are the same for both the nickel and cobalt complexes, the following equation is valid:

$$\frac{\Delta\nu_{Ni}^{contact}(i)}{\Delta\nu_{Ni}^{contact}(j)} = \frac{\Delta\nu_{Co}^{isotropic}(i)-\Delta\nu_{Co}^{dipolar}(i)}{\Delta\nu_{Co}^{isotropic}(j)-\Delta\nu_{Co}^{dipolar}(j)} \qquad (1)$$

where $\Delta\nu$ isotropic, contact and dipolar have their usual meaning[1] and where (i) and (j) refer to the ith and jth sets of equivalent ligand protons. Equation 1 is the basic equation of the so-called ratio method[1] by which experimentally observed $\Delta\nu_{Co}^{isotropic}(i)$ shifts may be factored into their $\Delta\nu_{Co}^{contact}(i)$ and $\Delta\nu_{Co}^{dipolar}(i)$ components. In the equation, $\Delta\nu_{Co}^{dipolar}(i) = \Delta\nu_{Co}^{dipolar}(j)\ [G_i/G_j]$ where G_i is the geometrical factor $[3\cos^2\theta_i - 1]/r_i^3$ relative to the ith nucleus in the dipolar expression, with r_i being the vector from the metal ion to the ith proton and θ_i being the angle between this vector and the molecular symmetry axis.

Since dipolar shifts are a sensitive function of the ligand proton position relative to the central metal ion, their evaluation affords a means of investigating molecular structure in solution. Using the three independent equations of type 1 which arise from the bipyO$_2$ proton sets (2,4–H), (3,4–H) and (5,4–H), the dipolar shift terms for the cobalt species have been evaluated assuming a D_3 molecular symmetry for the M(bipyO$_2$)$_3^{2+}$ cations *i.e.* only *ddd* or *lll* isomers. In this regard, reasonable values for the M–O distance (2.05 to 2.30 Å) and O–M–O angle (80° to 95°) have been simultaneously varied in order to find the set of geometrical factors which best satisfy the three independent equations of type 1 (see experimental section). Good agreement between the nickel and cobalt contact shift ratios could only be obtained by using the proton assignments shown in Figure 1.

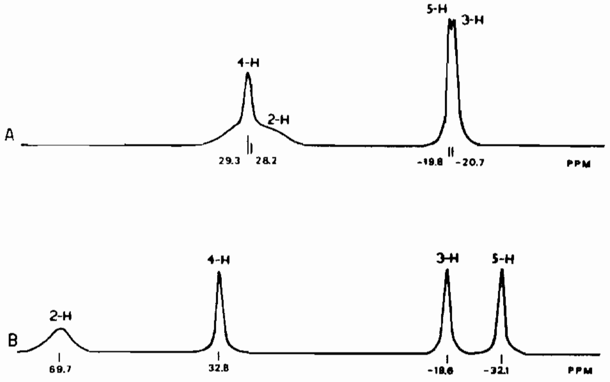

Figure 1. Pmr spectra of A) Ni(bipyO$_2$)$_3$(PF$_6$)$_2$ and B) Co(bipyO$_2$)$_3$(PF$_6$)$_2$ in d$_3$-acetonitrile at 26°C from internal TMS.

The final calculated $\Delta\nu_{Co}^{contact}(i)$ and $\Delta\nu_{Co}^{dipolar}(i)$ shifts together with their corresponding geometrical factors are tabulated in Table I. The « best set » of geometrical factors was obtained by assuming a M–O distance of 2.20 Å and O–M–O angle of 85°.[13] These geometrical factors correspond to only one possible ligand conformation (phenyl ring « tipping ») which,

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(10) G. N. La Mar and G. R. Van Hecke, *J. Am. Chem. Soc.*, *92*, 3021 (1970).

(11) I. Bertini and L. J. Wilson, submitted for publication.

(12) L. J. Wilson and I. Bertini, XIII I.C.C.C., Zakopane, Poland, article 137 (1970); 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970; and to be published.

(13) For this set of M—O and O—M—O values, the three $\Delta\nu_{Co}^{dipolar}$(4) solutions of equations 1 were calculated to be: —4 20, —3.70, —3.62 ppm. Changing the M—O distance to 2.10 Å or the O—M—O angle to 95° resulted in the following sets of solutions: —3.71, —2.91, —3.53 ppm and —3.15, —2.14, —3.29 ppm. For comparison purposes, by exchanging the assignments of 3— and 5—H for the Cobalt complex, no matter how one assignes the Nickel spectra, the solutions do have different signs. Leaving the present assignment for Cobalt and changing the assignment for the two Nickel signals (which differ of only 0.9 ppm) the best calculated values are —4.90, —2.87, —3.50 ppm. (M—O, 2.25 Å; O—M—O, 80°).

consequently, requires a M–O–N angle of 115° and an angle, α, between the two phenyl planes of 67°. The resulting M–O distance and M–O–N angle are in reasonably good agreement with the values[14] (2.10 Å and 121° respectively) found in the X-ray structural determination of the bis(2,4-pentanedionato)bis(pyridine-N-oxide)nickel(II) complex in which pyridine-N-oxide molecules function as monodentate ligands. On the basis of this structural comparision, it appears that the two pyridine-N-oxide fragments of the seven membered bipyO$_2$ chelate rings are accomodated in a relatively strain-free manner, probably a result of the ring « tipping » flexibility of the ligand.

Experimental Section

Preparation of the complexes. Bipyridine-N, N′-oxide was prepared as previously described.[15] The tris(bipyO$_2$)nickel(II) and cobalt(II) complexes were prepared as PF$_6^-$ salts. The appropriate MCl$_2$. 6H$_2$O metal salts and bipyO$_2$ ligand were combined in a 1:4 mole ratio in the minimum amount of boiling water necessary to achieve solution. Upon addition of a filtered water solution containing KPF$_6$ (mole ratio 2), a solid was immediately obtained which was recrystallized from an acetone-ether mixture. The yellow-green nickel and red cobalt salts were dried under vacuum over P$_4$O$_{10}$ for 14 hours at room temperature. *Anal.* Calcd. for C$_{30}$H$_{24}$F$_{12}$N$_6$O$_6$P$_2$Ni: C, 39.45; H, 2.65; N, 9.20. Found: C, 38.93; H, 2.53; N, 9.13. Calcd. for C$_{30}$H$_{24}$F$_{12}$N$_6$O$_6$P$_2$Co: C, 39.45; H, 2.65; N, 9.20. Found: C, 38.87; H, 2.69; N, 9.02.

Proton magnetic resonance spectra. Pmr spectra were obtained on a Varian DA–60 spectrometer operating at 60 Mc and 26°C. Spectra were recorded in d$_3$-acetonitrile and are referenced directly to internal tetramethylsilane (TMS). Proton resonance positions were measured operating in the HR mode employing standard sideband calibration techniques.

Calculations. The angle, α, between the two phenyl planes is determined by the O–O distance in the same bipyO$_2$ molecule; this distance, in turn, depends on the Ni–O distance and on the O–Ni–O angle. The following ligand skeleton distances have been used for the G$_i$ calculations: N–O and N–C, 1.335 Å; C–C, 1.375 Å; C$_6$–C$_{6'}$, 1.50 Å; C–H, 0.90 Å. All ligand angles have been taken to be 120°.

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(14) W. De W. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 7, 1552 (1968).

(15) G. M Badger and W. H. F. Sasso, *J. Chem. Soc.*, 617 (1956).