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42. ^{15}N-NMR. A Method for Assigning Structure in Complexes of Unsymmetrical *o,o'*-Dihydroxydiarylazo-Ligands

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(5. XII. 75)

Summary. The ^{15}N-NMR. parameters of some Pt(II)complexes of unsymmetrical *o,o'*-dihydroxydiarylazo-ligands are shown to be useful in the solution of subtle structural problems.

Introduction. – While azo complexes of a variety of metals are now extensively employed as dyestuffs [1], the techniques for detecting subtle differences in the molecular structure of metal complexes derived from unsymmetrical *o,o'*-dihydroxydiarylazo-ligands, such as **1**, are still limited. While *Schetty et al.* [2a] have been successful in applying ^{1}H-NMR. techniques in the study of 1:2-Co(III)-complexes containing two molecules of type **1**, in the study of square planar complexes of Pt(II) these methods have been found to be less exact (see preceeding paper [2b]). Indeed, the general problem of distinguishing between complexes such as **2a**[1]) and **2b** is not trivial especially in those cases where a suitable ^{1}H-'handle' is absent.

^{15}N-NMR. would seem to offer reasonable prospects for distinguishing between **2a** and **2b** since each of these isomers contains two distinct types of nitrogen atoms and we have prepared to this end the complexes **2a**, **2b** and **3a**, **3b** enriched in ^{15}N [2b] and measured their ^{15}N-NMR. spectra.

Experimental. – ^{15}N-NMR. spectra of the complexes were measured as saturated deuteriochloroform solutions containing 1×10^{-2}–4×10^{-2} M Cr(acac)$_3$ using a *Bruker* HX-90 spectrometer operating at 9.12 MHz in FT. mode. Compound **2b** was measured without the paramagnetic additive and was found to have the same chemical shift as in the doped sample. The effects of such a paramagnetic species on ^{15}N-resonances have been described [3].

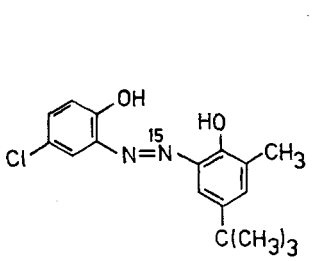
[1]) Compounds **2a** and **2b** correspond to structures **36a** and **36b**, compounds **3a** and **3b** to structures **37a** and **37b**, respectively, in the preceeding paper [2b].

Chemical shifts are relative to the ^{15}N-resonance of a saturated acidified solution of $^{15}NH_4Cl$ and are estimated to be ± 0.1 ppm.

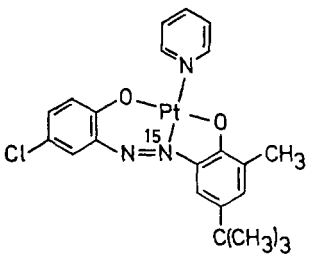
The syntheses of the compounds have been described by *Schetty et al.* [2b].

Results and Discussion. – While it is possible to prepare and isolate two materials whose analyses and physical properties suggest structures **2a** and **2b** the decision as to which material corresponds to **a** and which to **b** became trivial only after the ^{15}N-NMR. spectrum of compound **2a** was measured. In addition to the main band, two smaller resonances disposed symmetrically about this resonance were observed and these we assign as the ^{195}Pt-satellites (^{195}Pt, $I = 1/2$, natural abundance = 33.7%). Their separation (523 Hz) represents the value $^1J(^{195}Pt, ^{15}N)$. It has recently been shown [4] that, in ^{15}N-dodecylamine complexes of Pt(II) and Pt(IV), the one bond coupling between ^{15}N and ^{195}Pt is of the order of 220–350 Hz. Additionally, it has been suggested that the % s-character terms, α^2_{Pt} and α^2_N, in the *Fermi* contact expression for one bond couplings involving ^{195}Pt [4] [5] and ^{15}N [4] [6], make a major contribution to one bond couplings involving these nuclei.

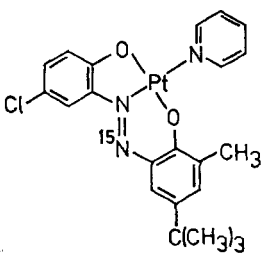
On this basis it is possible to assign structure **2b** to the complex whose ^{15}N-resonance appears at 363.2 ppm and structure **2a** to the isomer with the nitrogen absorption at 247.4 ppm, since it is expected[2]) that an sp^2-nitrogen directly bound to platinum would afford a value of $^1J(Pt, ^{15}N)$ in the range observed. No conclusions may be drawn from the failure to observe $^2J(Pt\text{-}N = {}^{15}N\text{-})$, in **2b**; however, we note that $^2J(Pt\text{-}N\text{-}{}^{13}C)$ in *trans*-[$PtCl_2(CH_2{=}CH_2)$(piperidine)] is only 14.6 Hz [7] and thus it is possible that two bond couplings of platinum to nuclei with small magnetic moments may not be large. It was not possible to observe the ^{195}Pt-satellites for **3a**[3]), however, as will be seen, their observation proved unnecessary.



1



2a



2b

The ^{15}N-resonance of **1** falls in the region expected for azo-compounds ($\delta^{15}N$ for **1** = 427.0 ppm; for *trans*-azo-benzene [8] = 486 ppm). The larger upfield coordination chemical shift, $\Delta\delta$, shown by **2a** (−179.6 ppm) relative to **2b** (−63.8 ppm) is under-

2) An increase in the value $^1J(Pt, ^{15}N)$ over that observed for the dodecylamine complexes is expected since the nitrogen atom in the azo complex is likely to approximate sp^2-hybridization while it is approximately sp^3 in the former case. An accurate prediction is, of course, not possible due to the dissimilarity of the complexes under consideration.

3) Since a) the platinum T_1 value in Na_2PtCl_4 is less than 1 sec., b) the platinum resonances of **2a** and **2b** have half widths of the order of several hundred Hz and c) the S/N ratio for the satellites in our spectrum would only have been 2–3/1, perhaps the satellites in **3a** were too broad to be observed.

standable if one accepts previous suggestions [8–10] concerning the importance of the mean triplet excitation energy term, ΔE, in the paramagnetic screening contribution, σ_P (equation 1).

$$\sigma_P \propto -(1/\Delta E). \tag{1}$$

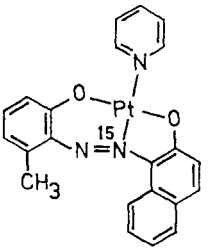
If, as has been suggested [11], the paramagnetic screening term, σ_P, is dominant, then:

$$\nu \propto H_0(1 - \sigma_P) \tag{2}$$

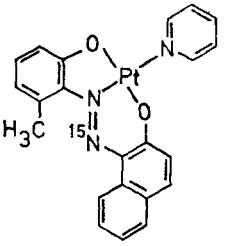
and low lying excited states, *e.g.* n $\rightarrow \pi^*$, will lead to deshielding of the ^{15}N-resonance. In structures such as **2a** the lone pair is coordinated to the metal, thus increasing the value for ΔE and inducing a high field shift in the nitrogen resonance. A shift of similar magnitude has been observed when quinoline-^{15}N ($\delta = 288.5$ ppm) is protonated to afford the quinolinium-^{15}N ion ($\delta = 159.4$ ppm; $\Delta\delta = -129.1$ ppm) [9].

In **2b** the lone-pair on the ^{15}N remains free and, while coordination of the adjacent nitrogen induces an upfield shift, the magnitude of $\Delta\delta$ is smaller. As $\Delta\delta$ for **2a** is so much greater than for **2b** it is not necessary to be able to observe the satellite lines associated with the lesser abundant isotope of platinum. The ^{15}N chemical shift is itself indicative of structure in these cases. It can be seen from the Table that in cases **2** and **3** the resonance position for each isomer is essentially constant suggesting that substituent effects on the ^{15}N chemical shifts are small relative to $\Delta\delta$.

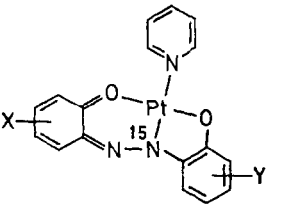
There is, in addition, some negative evidence available from the nitrogen chemical shift with reference to the possible contribution of hydrazone structures such as **4** to the molecular composite. The ^{15}N-resonance positions for *p*-X-Ph-^{15}N$_1$H-^{15}N$_2$=CHPh



3a



3b



4

Table. *^{15}N-NMR. data for the complexes*

Compound	Chemical Shift[a]	Coordination Chemical Shift[b]
1	427.0	0
2a	247.4	– 179.6
2b	363.2	– 63.8
3a	247.8	–
3b	368.2	

[a] Measured in ppm downfield from the ^{15}N-resonance of a saturated solution of $^{15}NH_4Cl$ (aq). The spectra were measured as $CDCl_3$ solutions.

[b] To high field of the ligand ^{15}N-resonance.

are $N_1 = 119.3$ and 128.0 ppm; $N_2 = 301.5$ and 295.7 ppm for $X = Cl$ and NO_2 respectively [11]. Thus we see that the hydrazine nitrogen N_1 appears at much higher field than the nitrogen resonances in our complexes by > 100 ppm suggesting that the azo-form **3** dominates in these molecules.

We conclude that ^{15}N-NMR. can be a powerful tool in the elucidation of molecular structure for such azo-complexes.

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43. Bemerkungen zur Synthese von 3-Aminotoluol-5-sulfonsäure und 2-Aminotoluol-3-sulfonsäure

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(25. VIII. 75)

Some comments on the synthesis of 3-aminotoluene-5-sulfonic acid and 2-aminotoluene-3-sulfonic acid. – *Summary.* Sulfonation of 3-nitrotoluene (**5**) yields predominantly the unsymetrical isomer 5-nitrotoluene-2-sulfonic acid (**7**), and lesser amounts of 5-nitrotoluene-3-sulfonic acid (**6**), previously reported as the major product. The desired 5-aminotoluene-3-sulfonic acid (**3**) was synthesized in preparative amounts from 6-aminotoluene-3-sulfonic acid (4) *via* the following sequence of reactions: diazotation and *Sandmeyer* replacement to 6-chlorotoluene-3-sulfonic acid (**13**), nitration of the sulfonyl chloride **14** under suitable conditions to give isomer free 6-chloro-5-nitrotoluene-3-sulfonyl chloride (**15**), hydrolysis to the sulfonic acid **16** and finally, simultaneous hydrogenolysis and reduction to **3**. The isomeric **7** was unequivocally prepared from 2-amino-5-nitrotoluene (**9**) *via* two routes: 1) diazotation, *Sandmeyer* thiocyanatation to 5-nitro-2-thiocyanatotoluene (**10**), Na_2S reduction to the di(2-methyl-4-nitro-phenyl)-disulfide (**11**), treatment with nitric acid and chlorine to give 5-nitrotoluene-2-sulfonyl chloride (**12**) and finally alkaline hydrolysis to **7**; 2) *Meerwein's* SO_2 treatment of the diazonium salt derived from **9** leads directly to **12** and thence to **7**.

2-Aminotoluene-3-sulfonic acid (**1**) was prepared from the key intermediate 3-amino-2-nitrotoluene (**18**) *via* the same two routes used to prepare **7** from **9**. Both reaction sequences provided 2-nitrotoluene-3-sulfonyl chloride, the hydrolysis product of which was reduced to **1**. Inter-