Application of Reverse Two-Dimensional $^1$H($^{15}$N} NMR Spectroscopy to the Characterization of Two Inorganic Compounds: (CO)$_5$Cr(R)NSNSNH

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Reverse 2D $^1$H($^{15}$N} NMR Spectra, Phosphane Complexes, Inorganic Ring System PS$_2$N$_2$, X-Ray

The inorganic ring system RPNNSNH linked to the [Cr(CO)$_5$] fragment [R = Bu (1), NH$_2$ (2)], has been studied by reverse two-dimensional, 2D $^1$H($^{15}$N} NMR spectroscopy. In solution, the exchange of the N—H hydrogen atoms is slow on the NMR time scale. Chemical shifts $\delta$($^1$H), $\delta$($^{13}$C), $\delta$($^{31}$P), $\delta$($^{15}$N} and coupling constants $J$($^{13}$P,$^1$H), $J$($^{31}$P,$^1$C), $J$($^{31}$P,$^{15}$N} are reported. In the case of 2, the reduced coupling constants $K$($^{15}$PN,$^1$H} and $K$($^{15}$PN,$^{15}$N} have the same sign.

The growing importance of $^{15}$N NMR spectroscopy in diverse areas of research is well recognized [1]. Following the introduction of polarisation transfer techniques like INEPT [2] a major progress in observing less abundant and low $\gamma$ spin 1/2 nuclei such as $^{15}$N has been achieved by indirect two-dimensional measurements of $^{15}$N via the observation of the $^1$H nuclei [3] (reverse 2D $^1$H($^{15}$N} NMR spectroscopy). Since the theoretical gain in sensitivity from these experiments as compared with direct $^{15}$N observation is given by ($\gamma^1$H/$\gamma^{15}$N$)^2$ (cf. INEPT with a gain of $\gamma^1$H/$\gamma^{15}$N$)^3$), diluted solutions in 5 mm tubes can be studied. This is particularly useful for compounds which are either sparingly soluble or can be obtained only in small quantities. Furthermore, as in other two-dimensional NMR experiments [4], additional information may be provided (e.g. on dynamic phenomena, on shift correlations, etc.) which, otherwise, would have to be deduced from a series of tedious one-dimensional experiments.

To our knowledge, the present study shows the first application of reverse 2D $^1$H($^{15}$N} NMR spectroscopy to inorganic compounds (cf. [15]). We have chosen the pentacarboxylchromium complexes 1 and 2 in order to demonstrate the considerable potential of this method in the investigation of inorganic nitrogen compounds. Thus the 2D $^1$H($^{15}$N} NMR experiments make it possible to

(i) determine the chemical shift $\delta$($^{15}$N};
(ii) observe the coupling constants $J$($^{15}$N,$^1$H} and $J$($^{31}$P,$^{15}$N} from the $^1$H NMR spectra of the $^{15}$NH or $^{15}$NH$_2$ groups, respectively (the $^{14}$NH contribution is totally suppressed); (iii) observe the coupling constant $J$($^{31}$P,$^{15}$N} and (iv) compare the relative signs of $J$($^{31}$P,$^{15}$N} for compound 2.

The NMR data obtained for the complexes 1 and 2 are given in Table I. 1 and 2 were isolated from the reactions of the phosphane complexes Cr(CO)$_5$[P(Bu)Cl]$_2$ [5] and Cr(CO)$_5$[PCl]$_3$ [6], respectively, with the salt K$_5$S$_2$[7]. The new cyclic phosphorus(III} compounds are stabilized by the electron-withdrawing [Cr(CO)$_5$] fragment. The proposed structures agree well with all IR, NMR and mass spectroscopic data [8]; the molecular structure of 1 was also determined by an X-ray structure analysis [9]. It was not possible, however, to decide on the

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basis of conventional $^1$H NMR spectroscopy whether rigid six-membered PS$_2$N$_3$ rings are present in solution or whether intra- or intermolecular exchange of the NH proton (to give tautomeric structures such as A and B) might be rapid on the NMR time scale.

Fig. 1 presents an expansion of the contour plot of the reverse 2D $^1$H{$^15$N} experiment for compound 1; the information on $\delta(^{15}$N) was obtained in less than 30 min. As the magnitude of the coupling constant $|J(^{15}$PN'H)| is very small (<1.5 Hz) the contour plot contains four cross peaks, representing $\delta(^{15}$N'H) (75.6 Hz) and $\delta(^{15}$P$^{15}$N) (60.2 Hz). The magnitude of $\delta(^{15}$N'H) is characteristic [10] of a rigid structure A or B. However, the $^1$H resonances are somewhat broadened, indicating that the rate of exchange processes approaches the NMR time scale.

Fig. 2 shows an analogous expansion of the contour plot for compound 2. Cross peaks for the NH and the NH$_2$ group, respectively, are readily assigned. The projection of the $^1$H NMR spectrum indicates that the $^{15}$NH resonances are broadened (as was observed for 1) with respect to the $^{15}$NH$_2$ resonances. However, both coupling constants $J(^{15}$PN'H) prove that $^1$H exchange is still slow.

It is obvious from Fig. 2 that two pairs of cross peaks are missing for the NH as well as for the NH$_2$ group (see Fig. 1 for comparison). This can be interpreted in terms of an intensity decrease of double quantum transitions in the AMX (HNP) and the A$_2$MX (H$_2$NP) spin systems, respectively. The pattern of the cross peaks for the NH and the NH$_2$ group is similar, suggesting that both $J(^{15}$PN$^{15}$N) and $J(^{15}$PN'H) have the same sign in the NH and NH$_2$ group. Cross peaks at low frequency in the F1 and in the F2 dimension are missing, as are the corresponding high frequency cross peaks in the two frequency axes. This pattern is expected if the reduced coupling constants $\gamma(^{15}$PN'H) and $\gamma(^{15}$PN$^{15}$N) have the same sign $[K(AB) = (4\pi^2/h)(|J(AB)|)^{2}/N_{A}N_{B}]$ in order to take the negative sign of $^{15}$N into account]. For a series of phosphorus(V)-nitrogen compounds it was found that $K(^{15}$PN$^{15}$N) < 0 [11]. If this is also true for compound 2, then $K(^{15}$PN$^{15}$N) < 0 which means $J(^{15}$PN$^{15}$N) > 0. This is in agreement with the results

<table>
<thead>
<tr>
<th>$^1$H NMR$^a$</th>
<th>Cr(CO)$_3$[P('Bu)NSNSNH]</th>
<th>Cr(CO)$_3$[P(NH)$_2$NSNSNH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$(NH)</td>
<td>4.26 (br)</td>
<td>4.26 d (br)</td>
</tr>
<tr>
<td>$J(^{1}$PN'H)</td>
<td>&lt;1.5</td>
<td>5.4</td>
</tr>
<tr>
<td>$\delta$(NH$_2$)</td>
<td>-</td>
<td>3.50 d (br)</td>
</tr>
<tr>
<td>$J(^{1}$PN'H)</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)</td>
<td>1.25 d</td>
<td>-</td>
</tr>
<tr>
<td>$J(^{1}$P'H)</td>
<td>16.6</td>
<td></td>
</tr>
</tbody>
</table>

$^{13}$C NMR$^b$

| $\delta$(C(CH$_3$)$_3$) | 23.5 d | -               |
| $J(^{1}$P$^{13}$C)      | 6.0    |                |
| $\delta$(C(CH$_3$)$_3$) | 40.4 d | -               |
| $J(^{1}$P$^{13}$C)      | 19.6   |                |
| $\delta$(CO)$_{eq}$     | 215.4 d| 214.7 d        |
| $J(^{1}$P$^{13}$C)      | 14.5   | 17.1           |
| $\delta$(CO)$_{ax}$     | 220.0 d| 219.3 d        |
| $J(^{1}$P$^{13}$C)      | 3.4    | 5.1            |

$^{15}$N NMR$^c$

| $\delta(^{15}$N)         | -259.3 | -311.0         |
| $J(^{1}$P$^{15}$N)       | 60.2   | 54.4           |
| $J(^{1}$N$^{15}$N)       | 75.6   | 77.0           |
| $\delta(^{15}$NH$_2$)    | -      | -313.0         |
| $J(^{1}$P$^{15}$N)       | -      | 30.4           |
| $J(^{1}$N$^{15}$N)       | 82.0   |                |

$^{31}$P NMR$^d$

| $\delta(^{31}$P)         | 131.7  | 105.6          |

Table I. NMR data (CDCl$_3$ solution).

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$^a$ Room temperature, rel. TMS;
$^b$ 0 °C, rel. TMS;
$^c$ room temperature, rel. external CH$_3$NO$_2$ in C$_6$D$_6$ solution;
$^d$ -30 °C, rel. ext. 85% H$_3$PO$_4$.
Fig. 1. Reverse 2D $^1$H($^{15}$N) NMR spectrum (expansion) of compound 1 (5 mm sample, ca. 5–10% in CDCl$_3$) at 295 K. The four cross peaks separated by $J(^{15}$N'H) (F2-scale) and $J(^{31}$P$^{15}$N) (F1-scale) are marked by arrows. Other intensities are non-relevant interferences from other frequencies.

The projection at the F1 axis shows the $^{15}$N NMR spectrum with $J(^{13}$P$^{15}$N).

Fig. 2. Reverse 2D $^1$H($^{15}$N) NMR spectrum (expansion) of compound 2 (5 mm sample, ca. 5–10% in CDCl$_3$) at 295 K. The cross peaks are separated by $J(^{15}$N'H) (F2-scale) and $J(^{31}$P$^{15}$N) (F1-scale). Note the missing cross peaks (see text) for the NH and NH$_2$ group. Other intensities are non-relevant interferences from other frequencies.

The projection at the F2 axis shows the $^1$H$^{15}$N satellite spectrum, demonstrating the total suppression of the $^{14}$NH resonance. The NH resonances are broadened with respect to the NH$_2$ resonances (see text).
for other phosphorus(V)-nitrogen compounds where it was observed that the reduced coupling constants \( K(\text{P}^{15}\text{N}) < 0 \), with few exceptions [11–13]. The data set available for \( J(\text{P}^{13}\text{N}) \) indicates that sign and magnitude of this coupling constant in the case of phosphorus(V)-nitrogen compounds is determined by the presence of the lone pair at the nitrogen atom and by the nature of the other substituents at phosphorus. It is apparent that quaternization of the phosphorus does not cause a change in the sign of \( J(\text{P}^{13}\text{N}) \) (as compared with \( \lambda \)-phosphorus-nitrogen compounds) if a weak polar phosphorus-element bond is formed [14].

The results obtained in this study for compounds 1 and 2 are encouraging and suggest further investigations, as the reverse 2D 'H{15}N NMR experiment is by no means restricted to molecules containing \( \text{NH}_n \) units. The 2D NMR experiment may even be based on much smaller coupling constants \( J(\text{N}^{15}) (n > 1) \) provided that an approximate value is known.

**Experimental**

**Preparation of the complexes**

A solution of 2 mmoles of either \( \text{Cr(CO)}_6[\text{P('Bu)NSNSNH}] \) [5] or \( \text{Cr(CO)}_5[\text{PCl}_3] \) [6] in 10 ml acetonitrile was added dropwise (over 15 min) to a cooled \((-40 \, ^\circ\text{C})\) suspension of 280 mg (2 mmol) \( \text{K}_2\text{SN}_2 \) [7] in acetonitrile. The reaction mixture was slowly brought to room temperature, stirred for 3 h and then evaporated to dryness under high vacuum \( (10^{-2} \, \text{bar}) \). The residue was extracted with 50 ml \( \text{CH}_2\text{Cl}_2 \); the solution was filtered over anhydrous \( \text{Na}_2\text{SO}_4 \), concentrated to ca. 5 ml and then chromatographed on TLC plates coated with silicagel (Merck, TLC-60, GF\(_{254}\), 0.5 mm).

\( \text{Cr(CO)}_5[\text{P('Bu)NSNSNH}] \) (1) was eluted using cyclohexane/\( \text{CH}_2\text{Cl}_2 \) \((7:3)\). Red, air-stable crystals, m.p. 85 °C, yield 155 mg (20%). IR: \( v(\text{CO}) 2069 \, \text{m}, 1961 \, \text{s}, 1946 \, \text{vs} \) (on pentane); \( v(\text{NH}) 3247 \, \text{m}, <3(\text{NH}) \) (on pentane); \( v(\text{NH}) 3247 \, \text{m}, <3(\text{NH}) \) (on pentane); \( v(\text{NH}) 3247 \, \text{m}, <3(\text{NH}) \) (on pentane).

\( \text{Cr(CO)}_5[\text{P(\text{NH})_2NSNSNH}] \) (2) was similarly isolated from the TLC plates using cyclohexane/\( \text{CH}_2\text{Cl}_2 \) \((3:7)\). Red-violet, air-stable crystals, m.p. 72–73 °C; yield 70 mg (10%). IR: \( v(\text{CO}) 2076 \, \text{m}, 1952 \, \text{vs} \) (on pentane); \( v(\text{NH})_2 3433 \, \text{m}, 3315 \, \text{m} \); \( v(\text{NH})_2 3433 \, \text{m}, 3315 \, \text{m} \); \( \delta(\text{NH}) 1551 \, \text{m} \) (KBr).

**NMR Spectra**

The \( ^{13}\text{C} \) and \( ^{31}\text{P} \) NMR spectra were measured using a Jeol FX 90Q spectrometer. The reverse 2D \( ^1\text{H}(^{15}\text{N}) \) NMR spectra were recorded with a Bruker AM 400 spectrometer, equipped with a selective \( ^1\text{H} \) probehead, modified for heteronuclear decoupling. Spectra were recorded using the pulse sequence [3] \( [\pi/2(\text{H})-\tau/2(^{15}\text{N})-t_1/2-\pi(\text{H})-t_1/2-\pi(^{15}\text{N})-\text{FID}(\text{H}, t_2)]_s \), where \( t = [2.J(^{15}\text{N})]^{-1} \) and \( t_1 \) is incremented according to the F1-spectral width \( \delta(^{15}\text{N}) \). This was selected first as \( ca. 5000 \, \text{Hz} \) in a wide sweep experiment for locating the \( ^{15}\text{N} \) resonance, and was then reduced to \( ca. 1500 \, \text{Hz} \) for obtaining more precise \( J(^{31}\text{P}(^{15}\text{N}) \) values \((\pm 1.5 \, \text{Hz}) \) and \( \delta(^{15}\text{N}) \) data \((\pm 0.1 \, \text{ppm}) \). For further information see Figs 1, 2 and Table I.

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b) A. G. Redfield, Chem. Phys. Lett. 96, 537 (1983);