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NMR STUDY OF THE ADDUCTS OF BF_3 AND $SbCl_5$ WITH ^{15}N-LABELED 1,3-DIMETHYLUREA.

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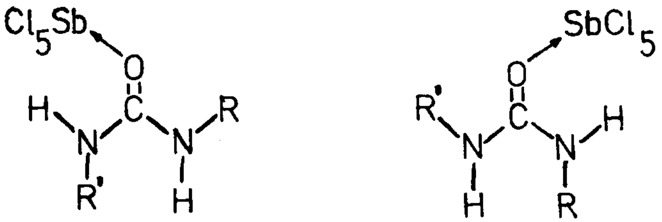
The question of O- versus N-coordination in Lewis acid adducts of amides and alkyl substituted ureas has been the subject of several NMR investigations during the last decade. (See e.g. Ref. 1 and references therein.) The observation of increased proton-proton coupling constants across the C-N bond upon adduct formation and slow rotation at room temperature in e.g. $DMF\cdot BF_3$ [2,6], $DMF\cdot BCl_3$[2,3,6], $DMF\cdot SbCl_5$[5,6] and $DMA\cdot SbCl_5$[4] is inconsistent with N-coordination.

O-coordination was also found in lactams,[7] and an X-ray investigation of $DMF\cdot SbCl_5$[8] showed O-coordination in the solid state.

In the case of alkyl substituted ureas evidence, mostly based on chemical reactions, suggested N-coordination in the boron trihalide[9] and PCl_5[10] adducts.

In a recent variable temperature PMR study of $SbCl_5$-N,N´-dialkylurea adducts a restricted exchange between two conformations was detected below room temperature.[11] The exchange was considered to be due to restricted rotation around the C-N bonds coupled with $SbCl_5$ exchange between two bonding positions at the carbonyl oxygen:



$SbCl_5$-exchange between the two nitrogen atoms is a less likely possibility, although it could not be completely ruled out. In order to investigate this further the present PMR study of ^{15}N-labeled 1,3-dimethylurea ($CH_3{}^{14}NHCO{}^{15}NHCH_3$) adducts was undertaken. It is known that direct ^{15}N-H couplings are dependent on the state of nitrogen hybridization[12,13] and will therefore give direct information about the bonding site in the adducts.

Results and discussion. Both adducts show the same type of methyl PMR as previously described for the $SbCl_5$ adduct[11], with two methyl signals below 0°. The NH region of the slow exchange PMR spectrum of the ^{15}N-labeled $SbCl_5$ adduct is shown in fig. 1 and the results are summarized in table 1. Direct ^{15}N-H couplings of the order of 90-100 Hz (sp^2-hybridized nitrogens) were observed for both slow exchange signals. Furthermore the two PMR signals from the ^{14}NH-protons were found to be of the same width, which indicates equal electric field gradients at nitrogen in both sites. The BF_3 adduct gave essentially the same results.

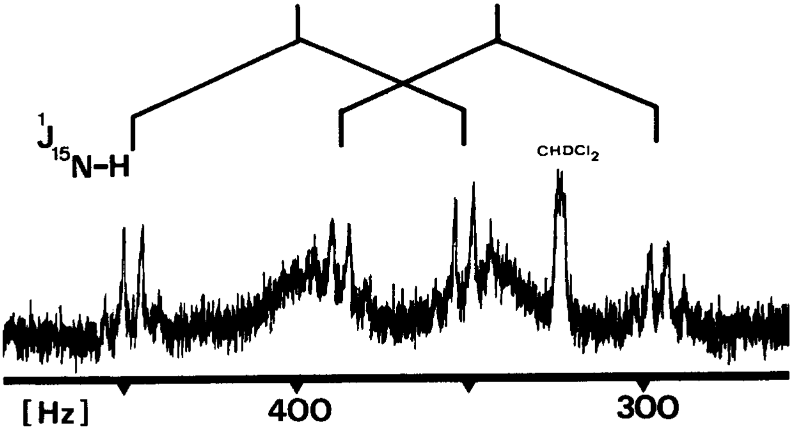


Fig.1 The NH region of the 60 MHz PMR spectrum of the ^{15}N-labeled adduct of $SbCl_5$ and 1,3-dimethylurea at -20°. The 1:3:3:1 structure of the signals arises from spin-spin coupling with the methyl groups ($^3J_{HH} \simeq 5$ Hz) and the broad signals are due to ^{14}NH protons. The scale is recalculated to TMS as reference by taking the shift of $CHDCl_2$ to be 323 Hz.

Table 1.

PMR parameters in Hz at 60 MHz for the NH PMR signals with estimated error limits

Acceptor	$^1J_{^{15}N-H}$ (low field)	$^1J_{^{15}N-H}$ (high field)	Separation
$SbCl_5$ (-20°)	96.5 ± 0.5	92.0 ± 0.5	57 ± 1
BF_3 (-35°)	98.0 ± 1.5	92.0 ± 1.5	46 ± 3

The observations are consistent with O-coordination but not with N-coordination, as the latter should lead to one sp^2- and one sp^3-type nitrogen ($\simeq$95 and $\simeq$75 Hz ^{15}N-H couplings, respectively), as well as different field gradients at the ^{14}N atom in the two conformers.

Experimental. The BF_3 adduct was prepared in a high vacuum line by standard methods to give an approximately 0.25 M CD_2Cl_2 solution. Solubility problems occured at low temperatures even at this concentration. BF_3 was repeatedly condensed onto solid NaF in vacuo to remove HF.[14] The $SbCl_5$ adduct was prepared as previously described[11] in a polyethylene glove bag (Instruments for Research and Industry) in a nitrogen atmosphere to give a 0.4 M CD_2Cl_2 solution. In both cases the donor-acceptor ratio was close to 1. Spectra were recorded immediately and after one weeks´ storage in a refrigerator without significant changes.

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