Warming solutions of either isomer **2a** or **2b** in deuterium oxide or various alcohols caused equilibration to a mixture of the two isomers. The pmr spectra of the α and β isomers (**2a** and **2b**) and the equilibrium mixture are shown in Figure 1 and indicate that the chemical shifts of the N–CH$_3$ and vinyl protons are different for the two isomers while the remainder of the spectra are very similar. The mass spectra of the α and β isomers (**2a** and **2b**) or the equilibrium mixture were identical and showed the loss of hydrogen bromide in the inlet system; the molecular ion peak was at m/e 199. The strongest peak in each spectrum was at m/e 170 and probably corresponded to 1-methyl-4-phenylpyridinium ion.

Either of the isomeric hydrobromides (**2a** and **2b**) or the equilibrium mixture was converted to the same amine **3** as evidenced by identical infrared and pmr spectra. The purified amine was recovered in 75–85% yield. The fragmentation pattern in the mass spectrum of the amine **3** was identical with that obtained from the hydrobromides.

Preliminary studies showed that the interconversion of **2a** and **2b** occurred very slowly at room temperature in solution in deuterium oxide but within minutes at 50°. At about 100° the two N–CH$_3$ resonance signals for the two isomers began to coalesce, showing that the rate of interconversion was comparable with the pmr time scale. The equilibration is hindered by addition of acid.

The isomers **2a** and **2b** must contain the same type of π-electron system because of the similarity in ultraviolet spectra. The skeletal arrangements of the two isomers must be the same or undergo rearrangement of a very unusual nature since the same base was formed from either isomer by thermal decomposition (identical mass spectra) or basic conditions (isolation experiments). The rearrangement of an unsaturated cyclic system such as **2** or **3** during salt formation or heating of a salt would logically occur by a carbonium ion mechanism. Thus, the decrease in ease of interconversion of **2a** and **2b** in an acidic medium also argues against **2a** and **2b** being skeletal isomers.

The experimental data seem to preclude an explanation of the isomerism of **2a** and **2b** based on structural differences and require a rationale based on stereoisomeric differences. The data are consistent with the hypothesis that the α- and β-hydrobromides differ only in the configuration of the ammonium nitrogen. The resonance of the methyl hydrogens of the β isomer at higher field suggests the assignment of structure **2b** in which the methyl is shielded by the π electrons of the double bond. This situation can be compared with the

relative chemical shifts of the two methyl signals of the pinenes, the high-field signal being assigned to the methyl group nearest to the unsaturation.[7]

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Robert E. Lyle, Charles R. Ellefson[8]
Department of Chemistry, University of New Hampshire
Durham, New Hampshire 03824
Received April 11, 1967

Nitrogen Hyperfine Splittings in the Electron Spin Resonance Spectrum of the Cr(NH$_3$)$_5$NO^{2+} Ion[1]

Sir:

The electron spin resonance spectrum of the Cr(NH$_3$)$_5$NO^{2+} ion in aqueous solution has been reported recently by several groups,[2-4] but neither Danon, *et al.*,[3] nor Meriwether, *et al.*,[4] observed ^{14}N hyperfine lines; Bernal, *et al.*,[2] reported the presence of hyperfine structure but were not able to resolve the spectrum. Trapp and Shyr[5] have also noted the presence of hyperfine ^{14}N structure in Cu(NH$_3$)$_6$Cl$_2$ in solid solution in diamagnetic lattices, but the spectra have not yet been analyzed.[6] We now report a well-resolved esr spectrum of Cr(NH$_3$)$_5$NO^{2+} in DMF solution which appears to be the first reported example of an NH$_3$ ligand (^{14}N) hyperfine splitting. The esr data, combined with MO calculations, provide considerable information concerning the electronic structure of the ion.

The spectrum was obtained using the compound [Cr(NH$_3$)$_5$NO][B(C$_6$H$_5$)$_4$]$_2$ which was prepared by directly interacting equivalent amounts of [Cr(NH$_3$)$_5$NO]Cl$_2$ and sodium tetraphenylborate, NaB(C$_6$H$_5$)$_4$, in aqueous solution; [Cr(NH$_3$)$_5$NO]Cl$_2$ was prepared by the method of Griffith.[7] The precipitate obtained was washed with cold water and then with ether, and analysis showed that it had the formula [Cr(NH$_3$)$_5$NO][B(C$_6$H$_5$)$_4$]$_2$. A magnetic susceptibility measurement proved the presence of one unpaired electron. The esr spectrum was obtained using a freshly prepared solution of this compound in DMF which was deaerated before use by passing through a stream of nitrogen gas. An experimental esr spectrum of Cr(NH$_3$)$_5$NO^{2+} ion is shown in Figure 1 (solid line). It consists of an intense central line due to ^{52}Cr which is further split by hyperfine interactions with ^{14}N of both NO and all five NH$_3$ groups. There is a considerable amount of overlapping of lines in the spectrum. Some of the lines due to the interactions with the ^{53}Cr nucleus (10% abundance) and the ^{14}N nuclei are seen in the lower field region of the spectrum. The high-field lines due to ^{53}Cr and ^{14}N interactions are not seen because the line widths have become greater; instead only one broad line due to the ^{53}Cr

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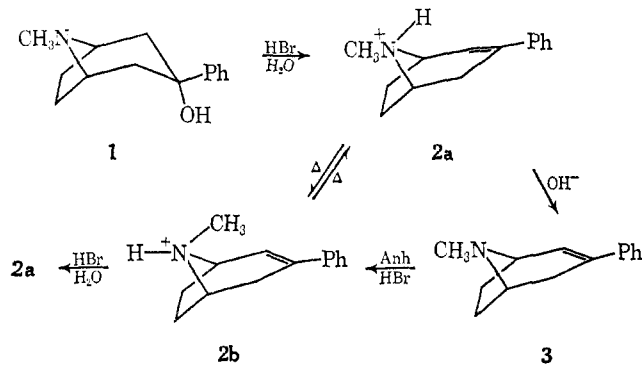(3) J. Danon, H. Panepucci, and A. A. Misetich, *J. Chem. Phys.*, **44**, 4154 (1966).
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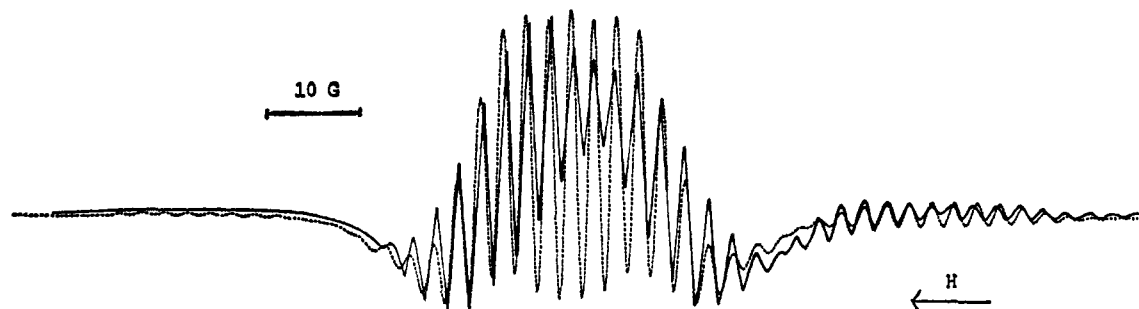(7) W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).

Figure 1. The second-derivative esr spectrum of $Cr(NH_3)_5NO^{2+}$ in DMF at room temperature is shown (solid line) along with spectrum calculated using the parameters of Table I (dotted line).

nucleus was obtained at higher gain, but this is not shown in the figures. A measurement in a frozen solution did not show any resolution of hyperfine structure.

The esr parameters obtained from the experimental spectrum are presented in Table I. The parallel and perpendicular components of the g values were obtained

Table I. Electron Spin Resonance Results for $Cr(NH_3)_5NO^{2+}$

	A value, gauss	
Esr parameter	This work	Previous work
g_{av}	1.980	1.980;[a] 1.978[b]
$g_{\|\|}$	1.945[c]	...
$g_{\perp}$	1.955[c]	...
$A_{iso}(^{53}Cr)$	25.01	21.7;[a] 25.4[b]
$A_{iso}(^{14}N$ from NO)	6.98	<3[b]
$A_{iso}(^{14}N$ from axial $NH_3)$	2.36	<2[b]
$A_{iso}(^{14}N$ from equatorial $NH_3)$	2.36	<2[b]

[a] Reference 2. [b] Reference 3. [c] Measurements from solid solution in ammonium chloride (polycrystalline). All other values are from DMF solution.

by a measurement using polycrystalline ammonium chloride doped with $[Cr(NH_3)_5NO]Cl_2$. The value of g_{av} ($= \frac{1}{3}(g_{\|\|} + 2g_{\perp})$) is in very good agreement with the g value obtained from the solution spectrum. The value for $A_{iso}(^{53}Cr)$ reported by Bernal, et al.,[2] does not agree with our value, but the anions were different.

The 6.98-gauss splitting has been assigned to the ^{14}N interaction from the NO ligand, in accordance with the similar values for $A_{iso}(^{14}N)$ in $Cr(CN)_5NO^{3-}$ (5.26 gauss)[8] and in $Cr(H_2O)_5NO^{2+}$ (6.45 gauss).[2-4,9] Also, the $A_{iso}(^{14}N)$ values for all NH_3 ligands appear to be equal which, as will be shown, leads to the most significant finding of this work. The calculated spectrum using the esr parameters given above (Table I) and an experimental line width is shown in Figure 1 (dotted lines). It was necessary to assume a line-width variation with the nuclear spin quantum number of ^{53}Cr in order to obtain a calculated spectrum which fits the experimental one closely. The resulting agreement provides confirmation of our assignment.

The esr results can best be interpreted by the energy level ordering $e(xz,yz) < b_2(xy) < e(\pi^*NO) < b_1(x^2 - y^2) \leq a_1(z^2)$ proposed by Manoharan and Gray.[10,11] The similar $A_{iso}(^{14}N)$ values arising from

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the nitrosyl group in all three chromium(I) nitrosyls, $Cr(CN)_5NO^{3-}$, $Cr(H_2O)_5NO^{2+}$, and $Cr(NH_3)_5NO^{2+}$, suggest that the ordering $e(xz,yz) < b_2(xy) < e(\pi^*NO)$ remains the same in all three complexes irrespective of the obviously different perturbations from the ligands CN^-, H_2O, and NH_3. In other words, the Cr–NO bond dominates the over-all ligand field. Moreover, these isotropic ^{14}N hyperfine splittings can be explained only it we assume that the unpaired spin has nitrogen s character. Since the b_2 orbital, in which the unpaired electron is located in the ground state, does not meet this requirement, we must have recourse to a configuration interaction treatment.[12] The σ NO orbital and the σ NH_3 (axial) orbital, which include a contribution from 2s (N), transform as the a_1 representation. Therefore the isotropic extrahyperfine splitting due to ^{14}N (σ NO) and ^{14}N (σ axial NH_3) can be explained by considering the excited configurations obtained by promoting an electron from a filled a_1 orbital to an unoccupied a_1 orbital. Similarly, the extrahyperfine splitting due to ^{14}N (equatorial σ NH_3) can be explained by promoting an electron from a filled b_1 orbital with nitrogen s character to the unoccupied one with the same symmetry.

The fact that the value of $A_{iso}(^{14}N$ from NO) for $Cr(NH_3)_5NO^{2+}$ (as well as that for $Cr(H_2O)_5NO^{2+}$) is larger than the $A_{iso}(^{14}N$ from NO) for $Cr(CN)_5NO^{3-}$ indicates that the energy separation involved in the two configurations concerned is much larger for $Cr(CN)_5NO^{3-}$ than for $Cr(NH_3)_5NO^{2+}$ and $Cr(H_2O)_5NO^{2+}$.

Equal isotropic hyperfine splittings (2.36 gauss) due to the ^{14}N interaction of equatorial and axial NH_3 ligands indicate that the $b_1(x^2 - y^2)$ and $a_1(z^2)$ molecular orbitals may have almost the same energies as indicated by the level scheme proposed by Manoharan and Gray[11] for chromium(I) nitrosyls. It is worth mentioning here that the isotropic extrahyperfine splitting constant due to ^{14}N in vanadyl porphyrin is about 2.8 gauss. This is very close to the value we have measured for ^{14}N from the NH_3 ligand. Thus we conclude that the $e(xz,yz) < b_2(xy) < e(\pi^*NO) < b_1(x^2 - y^2) \simeq a_1(z^2)$ ordering for the chromium(I) nitrosyls supports the esr results.

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P. T. Manoharan, H. A. Kuska, Max T. Rogers
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823