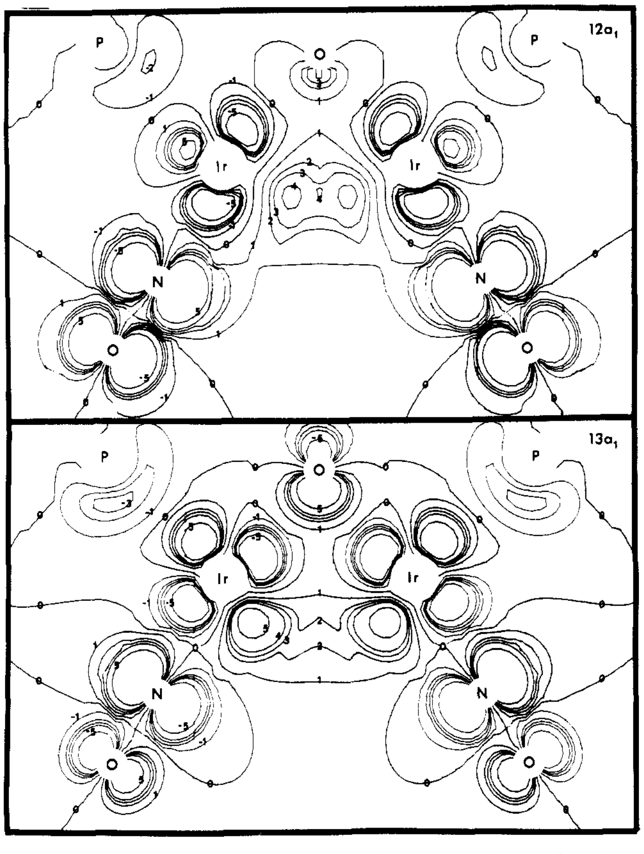

Figure 2. Contour maps of the $12a_1$ and $13a_1$ orbital wave functions for $Ir_2O(PH_3)_2(NO)_2$ in the molecular (xz) plane. The wave function changes sign as zero contours are crossed. A change of sign between two centers indicates an antibonding interaction; no change of sign, a bonding interaction. The contour values are 0, ±1, ±2, ±3, ±4, ±5 = 0, ±0.04, ±0.062, ±0.072, ±0.082, ±0.110 $(e/bohr^3)^{1/2}$, respectively.

Results and Discussion

Figure 1 shows our uppermost calculated energy levels and charge distributions for some of them. Not shown are lower levels of mainly O 2s and 2p, PH_3 $1a_1$, 1e, and $2a_1$, and NO 1σ, 2σ, 3σ, and 1π character. A fundamental question in nitrosyl chemistry is whether coordinated NO is best regarded formally as NO^0 or NO^+.[11] Figure 1 indicates that the present molecule is somewhat closer to $Ir^I–NO^0$ than to $Ir^0–NO^+$. If its formation is imagined to be from $Ir_2O(PH_3)_2$ and two NO fragments, the mainly NO 2π orbitals lie between the eight filled and two empty mainly Ir–Ir 5d combinations in energy. Hence the HOMO of the molecule, $12a_1$, has more NO than Ir character.

Comparison of individual orbital and total charge density contour maps shows, however, that the *net* in-plane Ir–Ir bonding in the molecule is essentially that arising from the 33% Ir character in the HOMO, $12a_1$. Figure 2 shows wave function maps for $12a_1$ and $13a_1$. $13a_1$ correlates with the orbital which *would* be the HOMO if the NO groups were removed. The Ir–Ir overlap in it corresponds closely to the classical bent bond which would complete square-planar coordination around each Ir. The presence of the nitrosyls, however, allows a more stable orbital to be occupied, with less Ir character but greater Ir–Ir overlap! The metal uses a 2:1 5d:6sp hybrid whose wave function lobes are slightly rotated from the fully bent toward the straight-bond alternative. As a result, the Ir–NO and Ir–PH_3 interactions are much less antibonding than in the $13a_1$ orbital. Moreover, the larger 6s and 6p functions allow better Ir–Ir overlap: note that the contour values increase toward the center of the Ir–Ir bond in $12a_1$, while they decrease in $13a_1$. The resulting bond is still quite bent, more so than any other reported to date.

In summary, the unique properties of NO as a ligand—in particular, its low-lying, partially filled 2π orbitals—are crucial in stabilizing and determining the exact nature of the substantially bent metal–metal bond. Furthermore, one might expect considerable use of metal s and p orbitals to be a common feature of bent metal–metal bonds, since overlap must be achieved over fairly long distances. These conclusions may aid in future designed syntheses of bent metal–metal bonds.

It is reasonable to ask whether these results would be significantly altered by relativistic[12] and valence bond (VB)[13] corrections. Relativistic corrections, by decreasing the Ir 5d–6sp splitting,[14] should lead to better d-sp hybridization and thus increased Ir–Ir overlap. Introduction of electron correlation at the VB level should somewhat localize the $12a_1$ electrons on the individual Ir centers. The net overlap of the two resulting VB orbitals would *probably* be less than in the MO picture. The *net* change in Ir–Ir bonding from both types of corrections is thus likely to be small, and none of the conclusions reached above should be affected.

Acknowledgment. We thank the NSF and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

Registry No. $Ir_2O(PPh_3)_2(NO)_2$, 26317-79-3.

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ESR Studies of Technetium Complexes: *trans*-Aquonitrosyltetraamminetechnetium(II) and Nitrosylpentachlorotechnetium(II)

George C. Yang,* M. W. Heitzmann, L. A. Ford,
and W. R. Benson

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Most technetium (Tc) complexes exhibit valence states of +5, +4, and +3.[1] The first low-valence Tc(I) cationic complex was reported by Eakins et al.[2] but formulated by them as $[Tc(NH_3OH)_2(NH_3)_3H_2O]Cl_2$. On the basis of chemical evidence and the determination of crystal structure by Radonovich and Hoard,[3] this was reformulated by Armstrong and Taube[3] as *trans*-$[Tc(NH_3)_4(NO)H_2O]Cl_2$. Technetium(I), with a $4d^6$ electronic configuration, is diamagnetic. In this work, we report the observation of ESR spectra of a technetium(II) ammine complex as well as a technetium(II) pentachloro complex. To our knowledge these are the first reported room-temperature ESR spectra of the known paramagnetic low-spin d^5 technetium species.[4]

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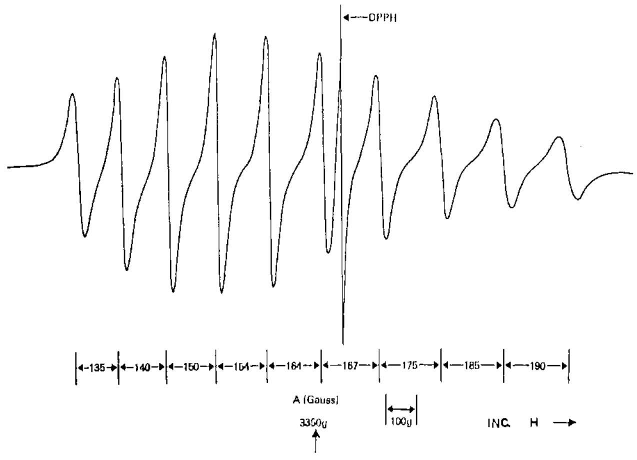

Figure 1. ESR spectrum of $[Tc(NH_3)_4(NO)H_2O]^{3+}$ at room temperature.

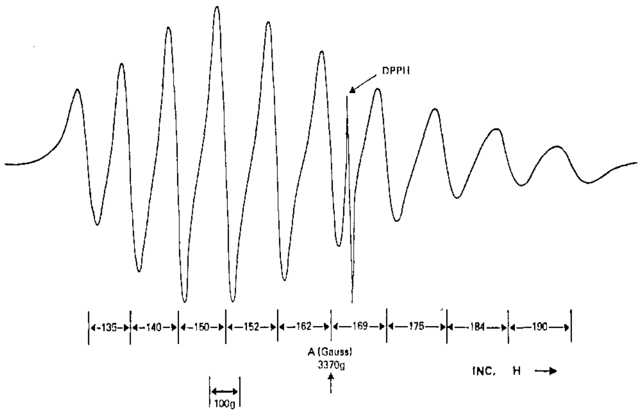

Figure 2. ESR spectrum of $[Tc(Cl_5)(NO)]^{2-}$ at room temperature.

Table I. Spin-Hamiltonian Parameters

	$[Tc(NH_3)_4(NO)H_2O]^{3+}$	$[Tc(NO)Cl_5]^{2-}$
$g_\parallel$	1.861 ± 0.039	1.891 ± 0.038
$g_\perp$	2.114 ± 0.030	2.104 ± 0.022
$A_\parallel$, G	296.6 ± 4.0	281.0 ± 4.0
$A_\perp$, G	108.8 ± 5.0	109.3 ± 5.0
g_{iso}	2.026 ± 0.001	2.024 ± 0.001
A_{iso}, G	165.4 ± 1.3	159.4 ± 1.4

Results

Upon oxidation of the pink species *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$ by potassium dichromate or ceric sulfate in perchloric acid, an ESR spectrum (Figure 1) with 10 hyperfine lines is observed at room temperature. Technetium-99 possesses a nuclear spin of $^9/_2$ and a large magnetic moment. End-point extrapolation of the titration curve, with dichromate as oxidizing agent and the ESR signal amplitude as a monitor for the paramagnetic Tc(II) complex concentration, shows that a one-electron oxidation took place.

When the pink species was warmed in concentrated HCl solution at elevated temperature (333 K), a new ESR spectrum appeared (Figure 2). Armstrong and Taube[3] have identified this species as a nitrosylpentachlorotechnetium(II) anionic complex, $[Tc(NO)Cl_5]^{2-}$, with chloride ligands replacing NH_3 and H_2O ligands.

Low-temperature (77 K) spectra for both complexes are shown in Figures 3 and 4. Their hyperfine and g tensors (Table I) are analyzed with use of the spin Hamiltonian

$$\mathcal{H} = H\cdot g\cdot S + I\cdot A\cdot S$$

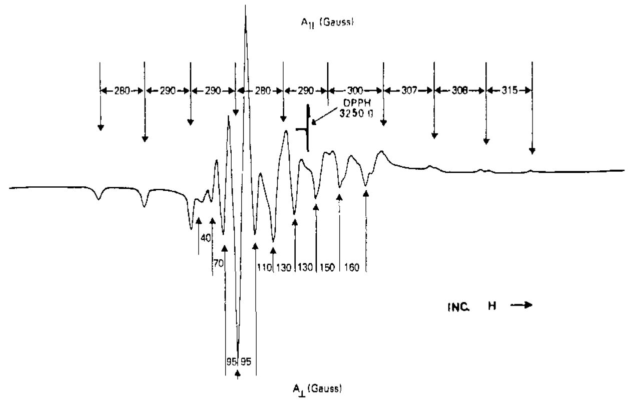

Figure 3. ESR spectrum of $[Tc(NH_3)_4(NO)H_2O]^{3+}$ at 77 K.

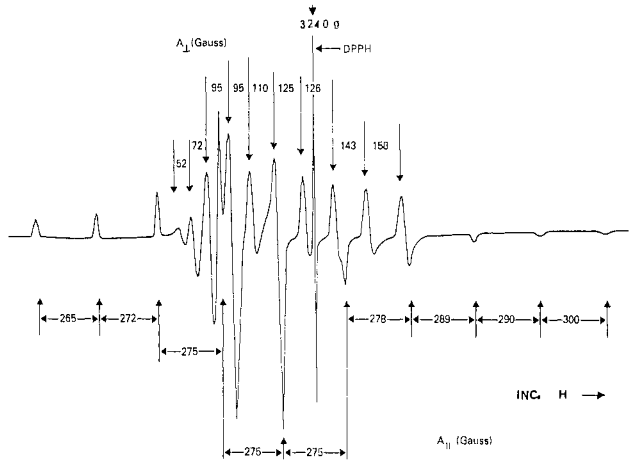

Figure 4. ESR spectrum of $[Tc(Cl_5)(NO)]^{2-}$ at 77 K.

Discussion

The *trans*-$[Tc(NH_3)_4(NO)H_2O]^{2+}$ complex, with Tc(I) in a $4d^6$ electronic configuration, is stable in 2 M perchloric acid solution. After air oxidation (storage over a long period of time) or chemical oxidation, the valence state of Tc(I) in the diamagnetic pink species is altered through a one-electron oxidation reaction to that of a low-spin $4d^5$ configuration. The low-temperature ESR powder spectral parameter indicates that the technetium ion is in an octahedral environment with a tetragonal distortion. There are five d electrons or one positive hole in the t_{2g} levels. The relative closeness between the parallel and perpendicular *g* factors can be accounted for by assuming that the magnitude of tetragonal distortion is much smaller than that of the spin–orbit coupling. Our ESR results also agree well with Armstrong and Taube's[3] conclusion that when the oxidation state of technetium is altered from I to II, the NH_3 ligands become more labile. Consequently, in a concentrated HCl solution, a new complex is formed with chlorides as ligands.

Experimental Section

The pink complex was prepared by the method of Eakins et al.[2] The hydroxylamine hydrochloride and potassium dichromate were ACS reagent grade. The Tc was obtained in the form of an aqueous solution of NH_4TcO_4 (0.30 M) from New England Nuclear Corp. ESR spectra were obtained with a Varian E9 spectrometer with a variable-temperature accessory.

Acknowledgment. Many helpful discussions with Dr. H. Kon, National Institute of Arthritis, Metabolism, and Digestive Diseases, National Institutes of Health, Bethesda, MD, are deeply appreciated.

Registry No. $[Tc(NH_3)_4(NO)H_2O]^{3+}$, 81753-12-0; $[Tc(NO)Cl_5]^{2-}$, 81753-13-1.

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