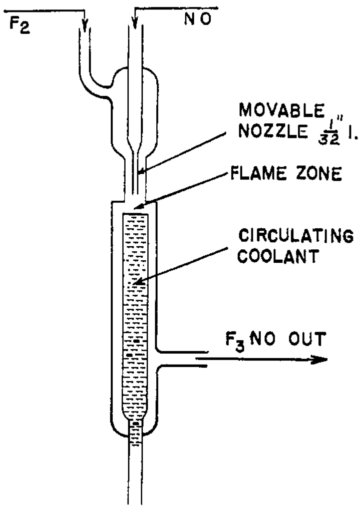

Figure 1. Flame reactor for continuous F_3NO production.

sitioned 0.005 in. below the shoulder. With F_2 and NO inputs of 500 ml/min each and coolant at $-125°$, 20% yields of F_3NO were produced at a continuous rate of 50 ml/min. As was the case with the previous reactor system, the residence time between generation of the NO–F_2 reaction mixture and product quenching for optimum operation was 15 msec.

Caution! Trifluoramine oxide is highly toxic and a powerful oxidant. All operations should be conducted in properly shielded hoods, and contact of reactants or products with organic materials must be avoided.

The mechanism of F_3NO formation probably involves the initial reaction of excess fluorine in the very hot (~2000°K) flame with FNO to produce an $F_2NO\cdot$ radical in either the ground or first excited state.

$$\text{FNO (or FNO*)} + \text{F}\cdot \rightleftarrows \text{F}_2\text{NO (or F}_2\text{NO}\cdot\text{*)} \qquad (4)$$

Reaction with a second fluorine would then produce the observed F_3NO.

$$\text{F}_2\text{NO (or F}_2\text{NO*)} + \text{F}\cdot \longrightarrow \text{F}_3\text{NO} \qquad (5)$$

We suggest that the intermediate radical is more likely to be the excited-state F_2NO^* on the following grounds. The ground-state $F_2NO\cdot$ radical (Figure 2) is, as predicted by Walsh[6] and verified in our own low-temperature spin resonance work,[7] slightly bent with the unpaired electron localized in a p orbital on the oxygen atom. Attack of fluorine on this radical would then occur on oxygen to yield a "hypofluorite" product, F_2NOF, which has never been observed, although its formation and subsequent rearrangement to F_3NO cannot be ruled out. On the other hand, the excited-state $F_2NO\cdot{}^*$, which should be energetically attainable at the 2000°K flame temperature, would be planar (Figure 2) with the unpaired electron localized on nitrogen to about the same extent as in NO.[6] Fluorination of this radical would then occur on nitrogen to give F_3NO directly.

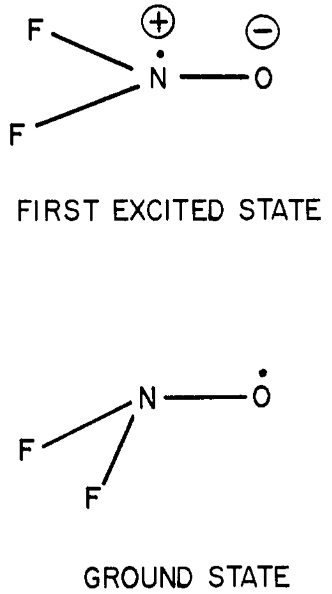

Figure 2. Configurations of the F_2NO radical.

Acknowledgment. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-30-069-ORD-2638.

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[6] A. D. Walsh, *J. Chem. Soc.*, 2306 (1953).

[7] Photolysis of F_3NO at $-196°$ produces the $F_2NO\cdot$ radical which exhibits a nine-line esr spectrum consisting of a fluorine-split triplet (a_F = 142.2 G), each component of which is further split by nitrogen into a triplet (a_N = 94.3 G). The fluorine hyperfine splitting is remarkably close to that observed for the isoelectronic, bent $CF_3\cdot$ radical [144.7 G: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965)]. On the other hand, the nitrogen hyperfine splitting of $F_2NO\cdot$ is more than ten times that of the planar $(CF_3)_2NO\cdot$ radical [8.2 G: W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, **87**, 802 (1965)]. A more complete account will be published separately by N. Vanderkooi, J. S. MacKenzie, and W. B. Fox.

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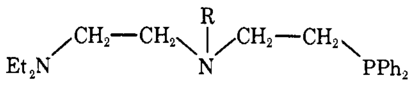
Spin-State Equilibrium in a Five-Coordinate Complex of Cobalt(II) Thiocyanate with an NNP Tridentate Ligand

Sir:

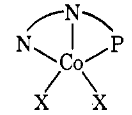
It has been found that in five-coordinate cobalt(II) and nickel(II) complexes the spin-pairing tendency parallels the nucleophilic reactivity constant (n^0) of the donor atoms,[1] as defined by Basolo and Pearson.[2] It has been shown for complexes of the type $Co(L)X_2$ (L = tridentate ligand; X = halogen, pseudohalogen) that the magnetic cross-over point occurs when the overall nucleophilic reactivity constant (Σn^0) is in the range 29–31.[1] In this range are the values for the donor sets NP_2X_2 in the spin-state isomeric complexes recently reported.[3]

With the "hybrid" ligands of general formula I we



$$\text{Et}_2\text{N}\diagup\text{CH}_2\text{—CH}_2\diagdown\overset{\text{R}}{\underset{}{\text{N}}}\diagup\text{CH}_2\text{—CH}_2\diagdown\text{PPh}_2$$

I, R = H, NNP; R = Me, Me—NNP



II

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[1] L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

[2] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 75.

[3] S. M. Nelson and W. S. J. Kelly, *Chem. Commun.*, 94 (1969).

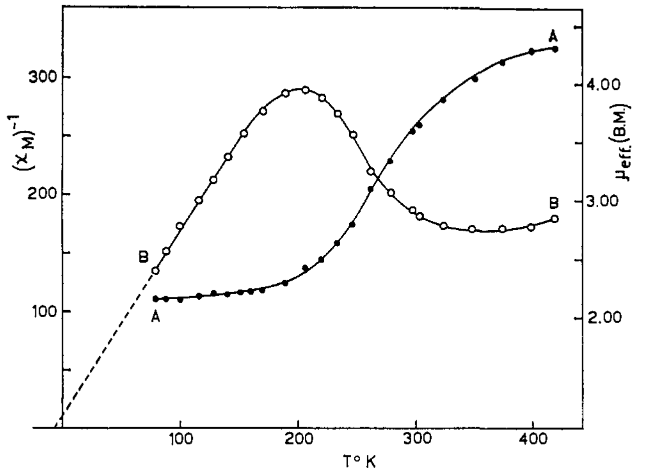

Figure 1. Variation of μ_{eff} (A, right-hand scale) and χ'_M (B, left-hand scale) with temperature for Co(NNP)(NCS)$_2$.

have isolated a series of complexes of general formula Co(L)X$_2$, with the donor set N$_2$PX$_2$ (II).[4] They have been found to be high-spin five-coordinate (μ_{eff} = 4.55–4.67 BM) when R = H, Me; X = Cl, Br, I (Σn^0 = 21.07–22.83) and when R = Me, X = NCS (Σn^0 = 28.29). The compound Co(NNP)(NCS)$_2$, however, shows an anomalous magnetic behavior as shown in Figure 1. Its magnetic moment (3.58 BM at 294°K) varies reversibly with temperature from 2.16 BM at 77°K up to 4.32 BM at 418°K (curve A). This suggests an equilibrium between a doublet ground state and a thermally accessible quartet state. If one takes as the high-spin limit the value of 4.47 BM found for Co(Me-NNP)(NCS)$_2$, the percentage of high-spin form at 294°K is about 53%. The linearity of the Curie–Weiss plot (curve B) up to about 160°K (Weiss constant = 7°) indicates that below this temperature the compound is almost completely in the low-spin form.

Reversible changes are also observed to take place in the electronic spectrum of the complex over the range 168–338°K. The low-temperature spectrum shows bands at about 6.8, 13.0 (sh), 18.5, and 21.2 kK, whereas at 338°K the spectrum exhibits bands at 6.4, 10.4, 15.5, and 20.5 kK. The latter pattern agrees in its general features with those observed for high-spin distorted five-coordinate cobalt(II) complexes.[5] We are unaware of any reported example of gradual interchange between distinctly different spectral patterns in magnetically anomalous cobalt(II) complexes.

In the ir spectrum (Nujol mull) recorded over the range 77–373°K, there are *two* ν_{N-H} bands, at 3170 and 3230 cm^{-1}, respectively (ν_{N-H} (free ligand) = 3300 cm^{-1}), whose intensity ratio varies reversibly with temperature (Figure 2): this would indicate that the spin isomerism is related to the interconversion of two distinct forms with different spin states. Much the same behavior is found for the doublet attributed to ν_{C-N} in N-bonded nonequivalent thiocyanate groups (Figure 2); this fact was also observed for the magnetically anomalous Fe(phen)$_2$(NCS)$_2$ and Fe(bipy)$_2$(NCS)$_2$ complexes,[6] and was related to the decreased M-NCS bond strength in the low-spin form.[7]

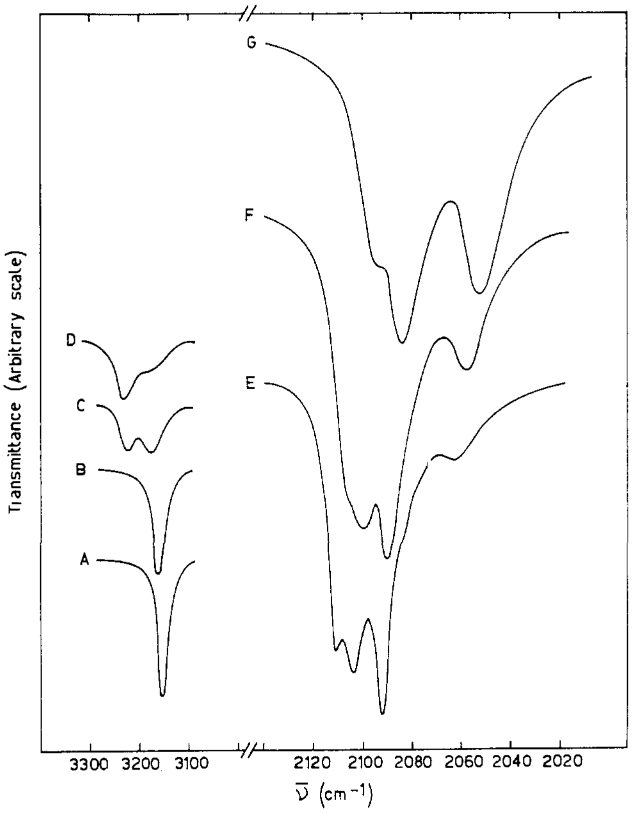

Figure 2. Infrared absorption frequencies of Co(NNP)(NCS)$_2$: N-H stretching at A, 77; B, 195; C, 298; and D, 373°K; C-N stretching (thiocyanate) at E, 77; F, 195; and G, 298°K.

The observed data could be accounted for if it is assumed that the spin-state variation is accompanied by a change in some of the structural parameters, with a corresponding change in the molecular geometry, as was suggested for the equilibrium $^4T_{1g} \rightleftarrows {}^2E_g$ in octahedral cobalt(II) complexes.[8] However, the present case is the first one of a five-coordinate cobalt(II) complex in which the interchange between the two forms has been detected by electronic and ir spectra. It is worth remembering that when a methyl group is substituted for the hydrogen on the central nitrogen atom a structural rearrangement occurs to give the high-spin five-coordinate complex Co(Me-NNP)(NCS)$_2$ which shows normal magnetic behavior.

An X-ray structural analysis on the complex Co(NNP)(NCS)$_2$ is in progress in this laboratory.

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[5] L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, 4, 1116 (1965); F. Lions, I. G. Dance, and J. Lewis, *J. Chem. Soc. A*, 565 (1967).

[6] W. A. Baker, Jr., and G. J. Long, *Chem. Commun.*, 368 (1965).

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