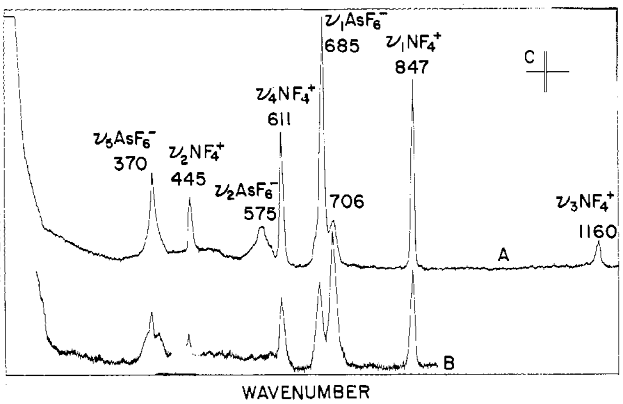

Figure 1.—Replotted Raman spectra of solid $NF_4^+AsF_6^-$ containing smaller (sample I, trace A) and larger (sample II, trace B) amounts of metal salts. C indicates spectral slit width.

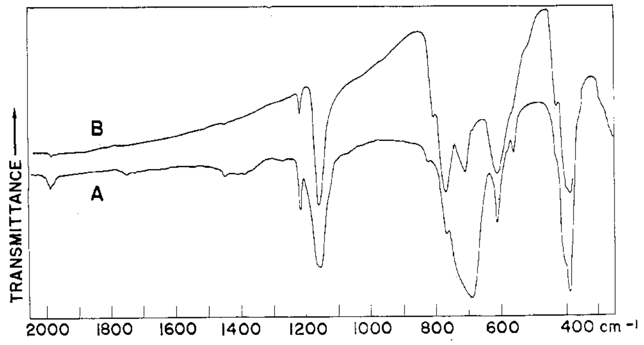

Figure 2.—Infrared spectra of solid $NF_4^+AsF_6^-$. Samples of traces A (AgBr pellet) and B (dry powder between AgCl plates) are identical with those of Figure 1.

tributed to the presence of the metal salts.[7] Furthermore, the previous reports[4] on the hydrolysis of NF_4^+ were confirmed in that NF_3 and O_2 were quantitatively evolved in a 2:1 mole ratio, and no evidence for the formation of nitrogen oxides or oxyfluorides[8] was found.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrogen trifluoride (Air Products) and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows or in the form of pressed AgBr disks. The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to −25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers.

Preparation of $NF_4^+AsF_6^-$.—Nitrogen trifluoride (180 mmol), AsF_5 (180 mmol), and F_2 (360 mmol) were heated in a passivated 150-ml Monel cylinder under autogenous pressure to 125° for 20 days. After removal of unreacted starting materials, the cylinder was opened in the glove box and contained about 2.88 g of a solid. About half of the solid had accumulated as a loose white powder (I) at the bottom of the reactor, the rest being distributed in the form of a yellowish layer (II) over the walls of the reactor. *Anal.* Calcd for 93.2 mol % of NF_4AsF_6, 5.8 mol % of $Ni(AsF_6)_2$, and 1.0 mol % of $Cu(AsF_6)_2$: N, 4.50; Ni, 1.21; Cu, 0.22; As, 27.50; total F, 66.59; hydrolyzable F, 6.11; NF_3:O_2 mole ratio, 2.0:1. Found for I: N, 4.64; Ni, 1.21; Cu, 0.23; As, 28.9; total F, 65; hydrolyzable F, 6.2; NF_3:O_2, 2.0:1. Found for II: N, 2.14; Ni, 2.95; Cu, 2.37; As, 28.0; NF_3:O_2, 2.02:1.

Elemental Analysis.—For N, Ni, Cu, As, and hydrolyzable F analyses, a weighted sample was hydrolyzed in a Teflon FEP U trap. The total amount of gas (NF_3 + O_2) was measured volumetrically; then NF_3 was separated from O_2 by fractional condensation at −210°, measured, and identified by infrared spectroscopy. The aqueous solution was analyzed for Ni, Cu, and As by atomic absorption, for As by X-ray fluorescence spectroscopy, and for hydrolyzable F both by $Th(NO_3)_4$ titration and by means of a fluoride electrode. For the total fluoride determination, the sample was fused prior to the F^- analysis using the Parr bomb technique (Na_2O_2 + starch).

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(7) Since the elemental analysis of the Ni- and Cu-rich sample showed an As content somewhat higher than that expected on the basis of the found N, Ni, and Cu values, we have explored the possible presence of a stable $As_2F_{11}^-$ anion in more detail. Solutions of the salt in HF showed only the ^{19}F nmr lines characteristic for NF_4^+, AsF_6^-, and HF, but no evidence for those previously reported (P. A. W. Dean, R. J. Gillespie, and R. Hulme, *Chem. Commun.*, 990 (1969)) for $As_2F_{11}^-$. When CH_3CN was used as a solvent, interaction with NF_4^+ occurred, resulting in a disappearance of the NF_4^+ signals but in a preservation of the AsF_6^- lines. Again no evidence for the $As_2F_{11}^-$ lines was obtained. Attempts to prepare $Cs^+As_2F_{11}^-$ under conditions similar to those used in the $NF_4^+AsF_6^-$ synthesis, *i.e.*, elevated temperature and pressure, produced exclusively $Cs^+AsF_6^-$. On the basis of these findings and the previously reported instability of $As_2F_{11}^-$ salts (P. A. W. Dean, *et al.*, *Chem. Commun.*, 990 (1969)), the presence of a stable $As_2F_{11}^-$ salt in our sample appears unlikely.

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Cobalt(II) Complexes of the Free-Radical Ligand Di-*tert*-butyl Nitroxide

BY DENNIS G. BROWN, THOMAS MAIER,
AND RUSSELL S. DRAGO*

Received March 10, 1971

In view of the interest in stable free radicals as spin labels and because of the potential insight about coordination of O_2 that could be gained by investigating free-radical ligands, we have become interested in the Lewis base di-*tert*-butyl nitroxide.[1] During the course of attempting to prepare various transition metal complexes of the ligand di-*tert*-butyl nitroxide[1] (DTBNO), $[(CH_3)_3C]_2NO$, a stable free radical, we felt it would be worthwhile to reinvestigate the properties of a previously reported compound $Co(DTBNO)_2Br_2$.[2] This complex is prepared quite easily by treating anhydrous $CoBr_2$ with neat DTBNO at room temperature and precipitating out the complex with petroleum ether (bp 30–60°). From elemental analysis and ultraviolet-visible spectroscopy, the compound resembled a conventional four-coordinate pseudotetrahedral cobalt(II) complex and the question immediately arose as to what the magnetic properties of this compound were. When $Co(DTBNO)_2Br_2$ was originally prepared, the room-

(1) This compound was prepared using a variation of the previously reported synthesis by A. K. Hoffmann, *et al.*, *J. Amer. Chem. Soc.*, **86**, 639 (1964). The donor properties toward hydrogen-bonding acids have been described by Y. Y. Lim and R. S. Drago, *ibid.*, **93**, 891 (1971).

(2) W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967).

temperature magnetic moment was reported to be 2.7 BM, which the investigators interpreted as corresponding to one unpaired electron.[2] Since the reported magnetic properties of this system and the spectral properties are apparently inconsistent, we undertook a detailed investigation of this compound to ascertain its electronic structure.

A room-temperature magnetic moment of freshly prepared $Co(DTBNO)_2Br_2$ was determined using the Gouy method. After correcting for the diamagnetic contribution, the molar susceptibility was found to be $\chi_m' = 7620 \times 10^6$ cgsu, which corresponds to an effective magnetic moment of 4.23 BM at 293°K. This value is somewhat low for tetrahedral cobalt(II) for which normal magnetic moments of 4.2–4.9 BM are found.[3] The theoretical value for a system containing three unpaired electrons on cobalt, which are not interacting with one unpaired electron on each ligand, *is obtained by summing the susceptibilities* or the expected moment is obtained from $\sqrt{\mu_{Co}^2 + 2\mu_L^2}$. Using μ = 4.2 for cobalt and 1.73 for the ligand leads to a predicted moment of 4.8 BM. If the MO description of the complex put the ligand electrons in degenerate MO's each of which was equally and mainly constituted of the two free-radical atoms, $\mu = \sqrt{(4.2)^2 + (2.8)^2} = 5.1$. A TIP correction of about 0.3 would lower these values slightly. In addition to this measurement on a solid sample, solution magnetic moments were determined in benzene and chloroform using the Evans method.[4] For these measurements, a JEOLCO C-60H high-resolution nmr spectrometer was employed. The results of these measurements at ambient temperatures were as follows: in chloroform, μ_{eff} = 3.9 BM; in benzene, μ_{eff} = 4.0 BM. When even a freshly prepared sample of the complex is dissolved in a well-dried solvent, it is found that a small amount of precipitate remains regardless of the care with which the complex is prepared and the accuracy of the elemental analysis of the sample. This and the uncertainty in the value of μ for the three unpaired electrons in d orbitals may account for the discrepancy between the predicted and observed moments.

It was felt that there could well be an equilibrium involving different spin states as the temperature was varied, so the temperature dependence of the magnetic suceptibility was determined. This experiment was carried out[5] over a temperature range of 300–10°K using a vibrating-sample magnetometer. Over this temperature range, the complex displays Curie behavior as shown in Figure 1. The magnetic moment does not change with temperature and has a value of 4.07 BM. For the instrument used in this work, the uncertainty in the determination of the gram-susceptibility is approximately ±1%.[5]

The electron spin resonance spectrum for a powder sample of the complex at liquid nitrogen temperature is shown in Figure 2. This is similar to the spectrum previously reported by Beck, *et al.*[2] Those workers assigned three components of the *g* tensor from the spectrum but were assuming a total spin of $S = 1/2$. Since $S \neq 1/2$, such a straightforward assignment of *g* values is not valid. The most unusual feature of the spectrum is the line width. In general, the line widths for tetrahedral cobalt(II) are considerably broader than this at a comparable temperature.[6] On the other hand, of course, the stable free radical gives a much sharper signal on the order of a few tenths of 1 G. Thus, the observed line width is characteristic of neither the radical nor a tetrahedral cobalt(II) ion but is somewhere between the line widths for the radical and cobalt(II) ion. The esr spectrum is quite unusual for a tetrahedral cobalt(II) complex. It resembles an $S = 1/2$ system with *g* values comparable to that expected for a tetrahedral cobalt(II) except that for $S = 3/2$ the resonance is expected at 2*g*. This could be a consequence of a very large zero-field splitting which might be expected if 10*Dq* for the radical and bromide differed significantly.

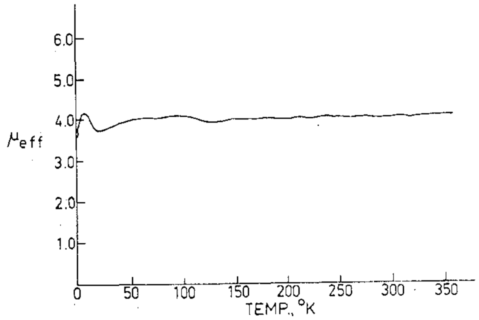

Figure 1.—Temperature dependence of the magnetic moment of $Co(DTBNO)_2Br_2$.

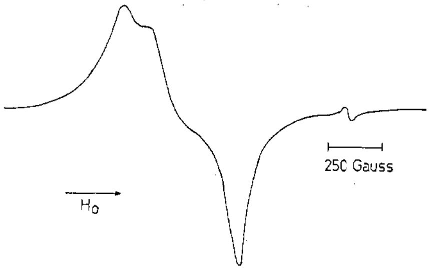

Figure 2.—The esr spectrum of $Co(DTBNO)_2Br_2$.

We decided to investigate the nmr spectrum of the complex to compare this with the free radical. The nmr spectrum of the complex exhibits contact shifts and line widths similar to those observed in the neat free radical. The methyl proton resonance in DTBNO comes at 7.7 ppm upfield from TMS with a line width of 4.5 ppm and the methyl resonance in the complex occurs at 5.6 ppm upfield from TMS with a line width of 3.2 ppm. Characteristic proton magnetic resonance line widths for tetrahedral cobalt(II) complexes for somewhat similar ligands are on the order of 0.4 ppm.[7] The observed proton relaxation times in $Co(DTBNO)_2Br_2$ are intermediate between those for the free radical and for normal tetrahedral cobalt(II) complexes.

It is possible that the cobalt ion in this complex could be reduced to a lower oxidation state which would make comparisons to conventional cobalt(II) complexes invalid. However, the ultraviolet–visible spectrum for this complex is very characteristic of tetrahedral cobalt(II) with a ${}^4A_2 \rightarrow {}^4T_1$ (P) transition at 6700 Å with the usual three components and the ${}^4A_2 \rightarrow {}^4T_1$ (F) transition in the infrared spectrum at 18,700 Å. From this information, average values of $\Delta = 3030$ cm^{-1} and $B' = 745$ can be calculated. Thus, in the $Co(DTBNO)_2Br_2$ complex, it is quite certain that the cobalt ion has a

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(3) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(4) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(5) The authors are very much indebted to George Rossman and Professor H. B. Gray for carrying out these measurements.

(6) J. C. Hempel and L. O. Morgan, *Inorg. Chem.*, **9**, 2064 (1970).

(7) B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 4597 (1966).

formal oxidation state of 2+. Using the average environment rule and $\Delta = 2950\ \text{cm}^{-1}$ for Br^- leads to a Δ value of 3110 for the nitroxide ligand.

Describing this material as cobalt(II) still leaves several possibilities with regards to the formulation of the electronic structure of the complex. Because of the uncertainties discussed, the magnetic data do not distinguish between three or five unpaired electrons in the complex. With a d^7 Co^{II}, the two remaining spins constitute either two separate uncoupled spins or are spin-paired with each other *via* a ligand–ligand interaction or occupy a degenerate MO each equally constituted of each set of ligand atoms giving an effective ligand triplet state. Since nitrogen hyperfine splitting is small compared to the observed line width, the five peaks expected from nitrogen hyperfine splitting if the electrons are in the degenerate MO described above would not be seen. We would not expect to see an esr resonance as sharp as that observed if if we had a C_{2v} cobalt(II) complex in which the ligands are spin paired by some ligand–ligand bond. This is the main evidence for eliminating this possibility. The nmr results are not as definitive as they might be. The small shift observed in the complex could conceivably be a pseudocontact shift of spin-paired diamagnetic ligands. However, the very broad resonance line which is observed suggests that the ligands are coordinated as essentially free radicals. In a series of $Co\{OP[N(CH_3)_2]_3\}X_2$ complexes, half-widths of the order of magnitude of 0.4 ppm were observed[7] and comparable widths would be expected here if a ligand–ligand bond existed. Of the three possible electronic structures proposed above, we can eliminate the one involving diamagnetic ligands but cannot distinguish between the other two possibilities. It would not be surprising if the expected zero-field splitting for a "triplet ligand" were not observed.

Several attempts were made at determining the crystal structures of $Co(DTBNO)_2Br_2$ and $CO(DTBNO)_2I_2$. For each complex, crystals were grown in two ways. To the solution of anhydrous CoX_2 (X = Br or I) in DTBNO was added dry benzene, the solution was filtered to remove any unreacted CoX_2, and crystals were grown by (a) slow evaporation of benzene or (b) vapor diffusion of low-boiling petroleum ether into the benzene solution. In all cases, small well-formed octahedral crystals formed. Precession and Weissenberg photographs indicated that all crystals were twinned, so no structure determination was attempted. For the iodide complex, it was determined from these photographs that the cell dimensions were $a = 9.68$, $b = 15.55$, and $c = 15.49$ Å with space group (from systematic extinctions) *Pnma* or *Pna*2_1.

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Vanadyl(IV)–Monothio-β-diketone Complexes. II. Bridged Compounds

BY B. JACK MCCORMICK* AND RONALD A. BOZIS

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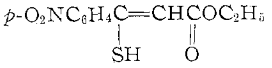
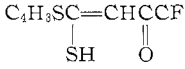
In a previous paper[1] three monomeric monothio-β-diketone (mtdk) complexes of VO^{2+} were reported which had properties consistent with square-pyramidal structures. Livingstone and coworkers,[2] on the other hand, have reported that a dimeric complex is formed from the fluorinated monothio-β-diketone Httmbs (see below) and VO^{2+}. We have been able to confirm Livingstone's preparation, as well as synthesize another complex that has similar properties. Reported here are the results of some studies directed toward the elucidation of the structures of these two complexes. The ligands used in this work were



$$p\text{-}O_2NC_6H_4\underset{\underset{SH}{|}}{C}{=}CH\underset{\underset{O}{\|}}{C}OC_2H_5$$

Hnebas



$$C_4H_3S\underset{\underset{SH}{|}}{C}{=}CH\underset{\underset{O}{\|}}{C}CF_3$$

Httmbs

Experimental Section

Reactants and Procedures.—Vanadyl(IV) sulfate dihydrate was used as received from Fisher Scientific Co. Ethyl 4-nitrobenzoylacetate and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione were supplied by the Aldrich Chemical Co. and Eastman Organic Chemicals, respectively. Solvents were distilled and deaerated with dry nitrogen before use.

Optical spectra were recorded with a Cary Model 14 spectrophotometer. A Cary Model 1411 attachment was used for the determination of diffuse-reflectance spectra. Infrared studies were carried out on Nujol or halocarbon mulls by using a Beckman IR-12 spectrometer and techniques similar to those described earlier.[1] Esr spectra, calibrated with DPPH, were obtained with a Varian E-3 instrument. Magnetic susceptibility measurements were made at room temperature by using a Gouy balance of standard design and $[Ni(en)_3]S_2O_3$[3] as the calibrant. The reported magnetic moments are corrected for ligand diamagnetic contributions.[4]

Molecular weights were determined with a Hitachi Perkin-Elmer Model 115 vapor pressure osmometer. The solvent was methylene chloride, and the measurements were made as quickly as possible after preparing the solutions. Elemental analyses were done by Chemalytics, Inc.

Syntheses.—Previously reported procedures were used for the preparation of the ligands Httmbs[5] and Hnebas.[6] The reaction between Httmbs and VO^{2+} was carried out as described by Livingstone and coworkers.[2] The melting point of the compound was 213° (215° reported previously[2]). Some additional properties of this compound are discussed below.

VO(nebas)$_2$.—A solution of VO^{2+} was prepared by dissolving 0.25 g (0.0013 mol) of $VOSO_4 \cdot 2H_2O$ in 0.5 ml of warm H_2O, to which was added 1.0 ml of ethanol after dissolution of the sulfate had taken place. To this solution then was added 0.50 g (0.002 mol) of Hnebas in 12.5 ml of absolute ethanol. Another solution was prepared by dissolving 7.0 g of $NaC_2H_3O_2 \cdot 3H_3O$ in 12 ml of water and diluting the resulting solution with 50 ml of absolute ethanol. A 2.5-ml amount of this acetate solution was then added slowly and with stirring to the warm Hnebas–$VOSO_4$ mixture. During the addition of the acetate a red gelatinous material formed which reacted further upon the completion of the acetate addition to provide a gold microcrystalline precipitate. The golden precipitate was collected on a filter, washed with water and petroleum ether (bp 60–90°), and dried over P_4O_{10}. The yield was 0.50 g, mp 170°. *Anal.* Calcd for $C_{22}H_{20}N_2O_9S_2V$: C, 46.24; H, 3.53; S, 11.22. Found: C, 46.71; H, 3.46; S, 11.22.

Properties of Complexes.—Both of the complexes are stable in air although some decomposition may take place over an extended period of time. In solution the complexes are subject to rather rapid decomposition and the rate of decomposition appears to be inversely related to the donor strength of the solvent. In general the complexes are only slightly soluble in noncoordinating solvents. In coordinating solvents such as pyr-

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(1) R. A. Bozis and B. J. McCormick, *Inorg. Chem.*, **9**, 1541 (1970).

(2) R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1179 (1966).

(3) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

(4) B. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960.

(5) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

(6) Z. Reyes and R. M. Silverstein, *J. Amer. Chem. Soc.*, **80**, 6373 (1958).