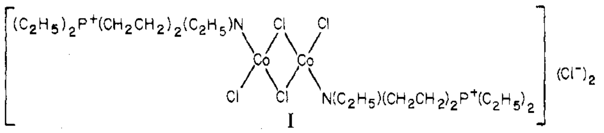
at 296°K: $\chi_M = 9199.6 \times 10^{-6}$, $\chi_M^{cor} = 9431.1 \times 10^{-6}$, $\mu_{eff} =$ 4.72 BM. Specific conductance [6.84×10^{-4} *M* (mononuclear unit) in purified absolute ethanol at 25°]: 5.38×10^{-5} ohm^{-1} cm^{-1}. Visible spectrum (reflectance, kK): 15.3 max, 16.8 s, sh, 17.9 w, sh, 20.2 vw, sh, 22.9 w.

Results and Discussion

When bis(2-chloroethyl)ethylamine hydrochloride was treated with diethylphosphine, using the method of Issleib[10] for the conversion of a 2-chloroethylamine to a 2-diethylphosphinoethylamine function, cyclization took place to give the substituted hexahydro-1,4-azaphosphorinum ring system. The product, hexahydro-1,4,4-triethyl-1,4-azaphosphorinium chloride, was isolated as its hydrochloride monohydrate. The analysis, melting point, solubility, and acidity of the compound are in accord with its formulation as a tertiary ammonium quaternary phosphonium salt. The ^{31}P nmr position is in the typical range for quaternary phosphonium salts[11] and indicates somewhat less shielding in the six-membered nitrogen-containing ring than in the simple tetraethylphosphonium ion. The infrared absorptions characteristic of the protonated tertiary amine and of water disappeared on conversion to the coordinated base in its cobalt(II) complex.

The free base $(C_2H_5)N(CH_2CH_2)_2P^+(C_2H_5)_2Cl^-$ can act as a ligand through nitrogen and might be compared to triethylamine.[12] Both of these form 1:1 complexes with cobalt(II) chloride, which contain pseudotetrahedrally coordinated cobalt(II) by the common criteria of ligand field spectrum and magnetic moment. Thus, both have the typically structured $^4A_2 \rightarrow {}^4T_1(P)$ (T_d) absorption, at 15.3 kK for the cationic ligand and at 16.0 kK for triethylamine.[12] The room-temperature magnetic moments of the cobalt complexes are 4.72 BM for the cationic ligand and 4.52 BM for triethylamine.[12] Both criteria indicate a somewhat smaller contribution to the average ligand field from the cationic ligand than from the uncharged amine, which is reasonable.

For the complex $CoCl_2 \cdot N(C_2H_5)_3$ to contain four-coordinate cobalt, it must be formulated as a dichloro-bridged dinuclear complex,[12] with negligible magnetic interactions at room temperature. The cationic ligand complex may be formulated similarly, as illustrated in structure I.



Alternatively, a nonelectrolyte zwitterionic structure $[L^+CoCl_3^-]$ might be considered. Such a structure has been reported for tetrahedral cobalt(II) complexes of various aminoaminium,[13] aminophosphonium,[14,15] and phosphinophosphonium[16] cationic ligands.

These zwitterionic complexes have a small degree of electrolytic conductance in polar solvents, due to partial solvolysis. In contrast, the complex reported here is highly conducting in absolute ethanol without a significant change in the absorption spectrum on dissolution.[17] A molar conductance of 157 ohm^{-1} cm^{-2} mol^{-1} is calculated for the dinuclear complex, well in excess of values for 1:1 electrolytes or for cobalt(II) chloride itself in this solvent.[18]

Registry No. $(C_2H_5)N(CH_2CH_2)_2P^+(C_2H_5)_2$ Cl^-, 36609-76-4; $[Co_2(L)_2Cl_4]Cl_2$, 36655-07-9.

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An X-Ray Photoelectron Spectroscopy Study of *N,N'*-Ethylenebis(benzoylacetoniminato)cobalt(II) and Its Oxygen and Nitric Oxide Adducts

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The nature of the bonding of molecular oxygen to metals in natural systems has long been of interest. Recent studies of coboglobin, hemoglobin with the iron replaced by cobalt, have shown that the cobalt-oxygen bond is quite similar to the iron-metal bond in hemoglobin.[1] Esr studies of various 1:1 cobalt-oxygen complexes have shown that the complexes may best be described as Co^{III}-O_2^- complexes,[2] that is, a superoxide ligand coordinated to a formally cobalt(III) species. The purpose of the studies reported here was to measure and compare the X-ray photoelectron spectra of Co(benacen) [benacen = *N,N'*-ethylenebis(benzoylacetonimine)] and its oxygen adduct in order to test the latter's formulation as a Co(III) complex. For similar reasons we have also examined the nitric oxide adduct of Co(benacen).

Experimental Section

All complexes were prepared by literature methods, the complex Co(benacen)pyO$_2$ [py = pyridine] by the method of Landels and Rodley,[3] the complex Co(benacen)NO by the method of Tamaki, *et al.*,[4] and the complex Co(benacen)pyNO$_2$ by the method of Clarkson and Basolo.[5]

The photoelectron spectra were taken on an AEI ES 100B spectrometer with an aluminum X-ray source (Kα = 1486.6 eV).

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Samples were prepared for the spectrometer by dissolving them in a small amount of methanol (pyridine for the O_2 adduct), pipetting 1 drop of the solution onto an aluminum sample plate, and evaporating the solvent. The C 1s peak from the benacen ligand was used as an internal binding energy reference. It was assigned a binding energy of 285.0 eV. The Co $2p_{3/2}$ spectra were obtained by counting the photoelectrons for 40 sec/channel at 0.2-eV kinetic energy intervals. The reported binding energies are the positions of the peak maxima and the half-widths are the full widths at half-maximum (FWHM).

Results and Discussion

The cobalt(II) Schiff base complex Co(benacen) has a binding energy (BE) of 780.0 ± 0.1 eV and a FWHM of 4.0 eV. A shoulder appears on the high-BE side of this peak indicating the possible presence of a Co(III) impurity.[6] The Co(III) complex Co(benacen)pyNO_2 has a BE of 781.4 ± 0.1 eV and a FWHM of 3.0 eV. This BE is 1.4 eV higher in energy than that of the Co(II) species. This increase in BE with increasing formal oxidation state is similar to that observed by Kramer and Klein for iron.[7] The measured Co $2p_{3/2}$ BE for the oxygen adduct Co(benacen)pyO_2 is 781.4 ± 0.1 eV, which is equal to the value for the cobalt(III)-nitro complex. The half-width was also 3 eV. This result indicates that the Co^{III}-O_2^- formulation proposed by esr studies[2] is correct. Rodley and Robinson have reported the X-ray structure of this complex.[8] They found a Co-O-O bond angle of 126 (2)° and a O-O distance of 1.26 (4) Å. These values are also indicative of a superoxide ligand as the superoxide ion has a bond length of 1.28 Å.

The X-ray structure of Co(benacen)NO indicates that the Co-N-O bond is bent with an angle of 122.9 (8)°.[9] Bent metal-NO bonds are thought to be indicative of NO^-. An examination of the X-ray photoelectron spectra show the BE of the Co $2p_{3/2}$ electrons is 780.9 ± 0.1 eV (FWHM = 2.8 eV), close to the value found for the cobalt(III)-nitro complex and the O_2 adduct. It thus seems that the best formulation is similar to the oxygen complex or Co^{III}-NO^-.

The N 1s region of the spectrum of Co(benacen)NO was examined. Two peaks are observed with an intensity ratio of 1:2 corresponding to the NO^- ligand and the benacen ligand, respectively. The BE for the NO^- was found to be 400.1 eV. This is in good agreement with the N 1s BE of 400.7 eV reported by Finn and Jolly[10] for the NO^- ligand in the complex $[Co(NH_3)_5NO]Cl_2$.

Registry No. Co(benacen), 36466-12-3; Co(benacen)(py)NO_2, 36609-90-2; Co(benacen)(py)O_2, 36643-07-9; Co(benacen)NO, 25848-52-6.

Acknowledgment. This work was partially supported by ARPA through the Northwestern University Materials Research Center and by a National Science Foundation Grant(GP-28134) for the purchase of the electron spectrometer.

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(6) A figure of the Co $2p_{3/2}$ spectra is available from the authors on request.

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Magnetic Properties of Oxovanadium(IV) Complexes of *N*-(Hydroxyalkyl)salicylidinimines

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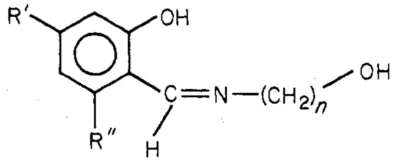
In recent years there has been considerable interest in the synthesis and magnetic properties of oxovanadium(IV) complexes with subnormal magnetic moments (referred to in this paper as subnormal complexes).[1-5] Recently Poddar, *et al.*,[6] have reported the synthesis of oxovanadium(IV) complex of *N*-(hydroxyethyl)salicylidinimine. They reported a room-temperature magnetic moment of 1.42 BM for this complex. Subsequently Kuge and Yamada[7] synthesized this compound independently and reported a room-temperature magnetic moment of 1.06 BM. Due to this anomaly in the literature it was of interest to repeat the work and study the magnetic properties of the complex in detail. In this note we report the magnetic properties of oxovanadium(IV) complexes of I.



I, R' = H, Cl, Br, NO_2, OCH_3
R'' = H, NO_2, OCH_3
n = 2, 3

Esr, infrared, and electronic spectral data of the complexes are also reported.

Experimental Section

Chemicals. Reagent grade salicylaldehyde and sodium acetate were obtained from J. T. Baker Chemical Co. Vanadyl dichloride was obtained from K & K Laboratories, Inc. 5-Chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-nitrosalicylaldehyde, 5-bromosalicylaldehyde, 3-nitrosalicylaldehyde, 5-nitrosalicylaldehyde, and propanolamine were purchased from Eastman Organic Chemicals. 3-Methoxysalicylaldehyde and 5-methoxysalicylaldehyde were obtained from Aldrich Chemical Co. Ethanolamine was the product of Matheson Coleman and Bell. All other chemicals used were of reagent grade quality.

Physical Measurements. Magnetic susceptibilities were determined by the Gouy method. Mercury tetrathiocyanatocobaltate was used as the standard. The diamagnetic corrections for the ligand and metal atoms were computed using a standard source.[8] The susceptibilities were corrected for TIP using a value of 50 × 10^{-6} cgsu. Electron spin resonance spectra were obtained with a Varian V-4502-12 X-band spectrometer using 100-kc modulation and a 9-in. electromagnet. Cylindrical quartz sample tubes and a Varian V-4533 cylindrical cavity were employed. For liquid nitrogen temperature a quartz dewar which fitted into the cavity was used. A minute sample of finely powdered diphenylpicrylhydrazil (DPPH) was used as a *g*-marker. Infrared spectra were obtained on a Perkin-Elmer Model 621 instru-

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