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Oxovanadium(IV) Complexes with Tridentate ONS Donor Ligands[1]

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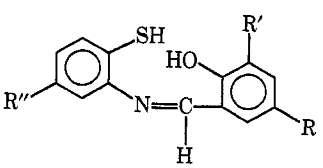
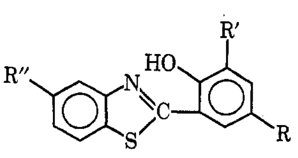
A new series of oxovanadium(IV) complexes of Schiff bases derived from substituted salicylaldehyde or 2-hydroxynaphthaldehyde and 2-aminothiophenol have been synthesized and characterized. The Schiff bases can coordinate through O, N, and S as bivalent tridentate ligands or can coordinate through O and N under proper conditions as monovalent bidentate ligands. The complexes are of the following types: (a) $VO(ON)_2$ and (b) $VO(ONS)\cdot nH_2O$ (where $n = 0$ or 1; ON represents bidentate Schiff bases with O and N donor atoms and ONS represents tridentate Schiff bases with O, N, and S donor atoms). The $VO(ON)_2$ complexes possess normal magnetic moments ($\mu_{eff} = 1.69$–1.86 BM) and the $VO(ONS)\cdot nH_2O$ complexes exhibit subnormal magnetic moments ($\mu_{eff} = 1.27$–1.28 BM) at room temperature. The magnetic susceptibilities of the VO(ONS) complexes have been measured at three points and the magnetic data support an antiferromagnetic exchange. The magnetic and spectral properties of the analogous copper(II) complexes are also discussed.

Introduction

Oxovanadium(IV) and copper(II) ions resemble each other magnetically in having one unpaired electron in their complexes. The symmetries of the unpaired electrons are, however, significantly different. In copper(II) the unpaired electron is derived from the e_g set whereas for oxovanadium(IV) the unpaired electron is derived from the t_{2g} set. Copper(II) complexes with antiferromagnetic exchange are well known and a source of continuing interest and controversy.[2] On the contrary, only a few examples are known with oxovanadium(IV) complexes.[3–6] Muto[7] has studied the copper(II) complexes of Schiff bases of 5-substituted *N*-(2-thiophenyl)salicylidenimine and established an interesting fact that the compounds all have effective magnetic moments above 1.73 BM at room temperature. This is in contrast to the known subnormal behavior of 5-substituted *N*-(2-hydroxyphenyl)salicylidenimine complexes of copper(II). In order to assess the role of sulfur further in metal complexes of this type, we have investigated oxovanadium(IV) complexes of Schiff bases derived from substituted salicylaldehyde or 2-hydroxynaphthaldehyde and 2-aminothiophenol. The Schiff bases can coordinate through O, N, and S as bivalent tridentate ligands (I) or under some conditions can coordinate through O and N as monovalent bidentate ligands (II) resulting in both normal and subnormal oxovanadium(IV) complexes.



I



II

R = H, Cl, Br, NO_2
R′ = H, Cl
R″ = H, Cl

To date only few oxovanadium(IV) complexes with sulfur donor ligands are known and all of them are synthesized from bidentate ligands.[8] There is no report of any oxovanadium(IV) complex with a tridentate ligand containing a sulfur donor atom and our complexes are the first report of such oxovanadium(IV) complexes. Tridentate dibasic ligands have received considerable attention recently due to the possibility of dimerization leading to metal complexes with anomalous magnetic properties.[9]

Experimental Section

Chemicals.—Reagent grade salicylaldehyde and purified reagent grade vanadyl sulfate dihydrate were obtained from Fisher Scientific Co. Vanadyl dichloride was obtained from K & K Laboratories, Inc. Cupric acetate monohydrate was a product of Mallinckrodt Chemical Works. 2-Aminothiophenol, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3-nitrosalicylaldehyde, and 5-nitrosalicylaldehyde were purchased from Eastman Organic Chemicals Co. 2-Hydroxynaphthaldehyde and 5-chloro-2-mercaptoaniline hydrochloride were obtained from the Aldrich Chemical Co., Inc. Other chemicals used were of reagent grade quality.

Syntheses of the Complexes. Preparation of VO(5-Cl-Sal-2-aminothiophenol)(H_2O).—The Schiff base was prepared from 0.01 mol of 5-chlorosalicylaldehyde by following a similar procedure as described by Muto;[7] yield 70%. The Schiff base is a yellow powder and melts sharply at 130°. Schiff base (0.005 mol) was dissolved in 20 ml of ethanol and 0.005 mol of vanadyl dichloride in 5 ml of ethanol was added. This mixture was stirred at room temperature for 1 hr and then refluxed for 12 hr. The greenish yellow precipitate was collected on a filter, washed several times with water, ethanol, and ethyl ether, and then dried at 80° overnight in a vacuum desiccator. The yield is about 70% based on vanadyl dichloride. The compound turned green at 200° and did not melt at 300°.

Another method of preparation is to make the complex directly without isolation of the Schiff base. 2-Aminothiophenol (0.005 mol) and 0.005 mol of 5-chlorosalicylaldehyde were added to 20 ml of ethanol and stirred on a magnetic stirrer for 15 min. Then 0.005 mol of vanadyl dichloride in 5 ml of ethanol was added dropwise to the solution. After the addition of vanadyl dichloride, the mixture was stirred magnetically for 1 hr and then refluxed

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[1] Based in part from the M.S. thesis of C. C. Lee submitted to the Graduate School of North Texas State University. Presented at the combined Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 4, 1970.

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TABLE I

ANALYTICAL DATA OF OXOVANADIUM(IV) AND COPPER(II) SCHIFF BASE COMPLEXES

Complex	Stoichiometry	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
VO(Sal–2-aminothiophenol)$_2$	$C_{26}H_{16}N_2O_3S_2V$	60.11	60.03	3.08	3.05	5.39	5.27
VO(Sal–2-amino-4-chlorothiophenol)$_2$	$C_{26}H_{14}N_2O_3S_2Cl_2V$	53.06	52.93	2.38	2.39	4.76	4.58
VO(5-Cl-Sal–2-aminothiophenol)$_2$	$C_{26}H_{14}N_2O_3S_2Cl_2V$	53.06	52.66	2.38	2.46	4.76	4.72
VO(5-NO$_2$-Sal–2-aminothiophenol)$_2$	$C_{26}H_{14}N_4O_7S_2V$	51.23	51.40	2.29	2.23	9.19	8.95
VO(3-NO$_2$-Sal–2-aminothiophenol)$_2$	$C_{26}H_{14}N_4O_7S_2V$	51.23	51.28	2.29	2.51	9.19	9.44
VO(5-Cl-Sal–2-aminothiophenol)(H$_2$O)	$C_{13}H_{10}NO_3SClV$	45.02	44.38	2.88	2.62	4.04	3.95
VO(5-Br-Sal–2-aminothiophenol)	$C_{13}H_8NO_2SBrV$	41.82	41.95	2.14	1.78	3.75	3.58
VO(5-NO$_2$-Sal–2-aminothiophenol)	$C_{13}H_8N_2O_4SV$	46.01	45.31	2.35	2.43	8.26	8.78
VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H$_2$O)	$C_{17}H_{13}NO_3SV$	56.35	57.07	3.59	3.55	3.86	3.81
Cu(Sal–2-aminothiophenol)	$C_{13}H_9NOSCu$	53.70	53.53	3.09	3.00	4.81	4.70
Cu(2-hydroxynaphthaldehyde–2-aminothiophenol)	$C_{17}H_{11}NOSCu$	59.91	59.14	3.23	3.26	4.11	4.20

overnight. The resulting greenish yellow product was filtered, washed, and dried in the same manner as above.

Vanadyl sulfate dihydrate can be used as a substitute for vanadyl dichloride. However, in this case, a weak base such as sodium acetate trihydrate and an 80% ethanol–20% water solution are required. The mixture was stirred and refluxed overnight and then the same product could be obtained.

Preparation of VO(5-Br-Sal–2-aminothiophenol).—The Schiff base was prepared according to the method reported by Muto.[7] Schiff base (0.01 mol) was dissolved in 30 ml of anhydrous methanol and filtered. To this solution, 0.01 mol of vanadyl sulfate dihydrate and 0.02 mol of sodium acetate trihydrate in 5 ml of water were added. The mixture was stirred magnetically for 1 hr and then refluxed overnight. The resulting greenish yellow compound was filtered, washed with water and methanol, and dried at 80° in a vacuum desiccator. The complex did not melt up to 250°.

Preparation of VO(5-NO$_2$-Sal–2-aminothiophenol).—This complex was synthesized following the same method as described for VO(5-Cl-Sal–2-aminothiophenol) using 5-nitrosalicylaldehyde instead of 5-chlorosalicylaldehyde.

Preparation of VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H$_2$O).—2-Hydroxynaphthaldehyde (0.86 g, 0.005 mol) and 0.62 g (0.005 mol) of 2-aminothiophenol were added to 50 ml of 95% ethanol and stirred magnetically for 0.5 hr. To this solution an ethanolic solution of sodium acetate trihydrate (0.01 mol, 1.36 g) was added followed by an ethanolic solution of vanadyl dichloride (0.005 mol in 10 ml). The resulting mixture was stirred magnetically for 1 hr and then refluxed for 2 hr, which resulted in the separation of greenish yellow precipitates. These were suction filtered, washed with 95% ethanol, and dried *in vacuo* overnight; yield 70%, mp >250°.

Preparation of VO(ON)$_2$ Complexes.—The complexes of the series VO(ON)$_2$ were prepared by following the general method. 2-Aminothiophenol (0.01 mol) and 5-substituted (or 3-NO$_2$) salicylaldehyde (0.01 mol) were added to 25 ml of absolute ethanol. The solution was stirred on a magnetic stirrer for 4 hr at 40°. The product was filtered and washed with ethanol and then dried in a vacuum desiccator at 25°; yield ~85%. These Schiff bases are white or pale yellow. Schiff (0.01 mol) base was dissolved in 25 ml of ethanol and to this 0.005 mol of vanadyl dichloride in 5 ml of ethanol was added. This mixture was refluxed overnight. The greenish yellow powders formed were collected on a filter, washed several times with water, ethanol, and ethyl ether, and dried at 80° under vacuum for 15 hr. In some cases, the simple washing process could not remove all the impurities. Therefore, the resulting complexes were boiled with 40% water–60% ethanol solution for several hours. The yield for all the complexes was about 70%. Vanadyl sulfate dihydrate with a weak base (sodium acetate trihydrate) can be used in place of vanadyl dichloride. However, a 4:1 ethanol–water solution is required as solvent. Attempts to prepare a VO(ON)$_2$ type complex from 2-hydroxynaphthaldehyde–2-aminothiophenol always produced impure products.

Preparation of Cu(Sal–2-aminothiophenol).—This complex was prepared according to Muto's procedure.[7]

Preparation of Cu(2-hydroxynaphthaldehyde–2-aminothiophenol).—2-Hydroxynaphthaldehyde (1.03 g) and 0.75 g of 2-aminothiophenol were added to 150 ml of absolute alcohol and stirred magnetically for 0.5 hr. The resulting orange-yellow solution was filtered and the filtrate was added to an aqueous solution of copper(II) acetate monohydrate (1.19 g in 15 ml). The resulting mixture was stirred magnetically for 12 hr. The green precipitates formed were filtered off, washed with ethanol and a 1:1 ethanol–water solution, and dried *in vacuo*. This was then dissolved in a minimum amount of pyridine and to the pyridine solution water was added and the brown monopyridine adduct of Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) was precipitated. This was filtered off, washed with ethanol, and finally dried *in vacuo* at 150° for 15 hr. Complete elimination of pyridine takes place at this temperature.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by the North Texas State University Analytical Services and Galbraith Laboratories, Knoxville, Tenn.

Melting Point.—The melting points of the complexes are uncorrected and were determined in sealed tubes using a Thomas-Hoover capillary melting point apparatus.

Magnetic Susceptibilities.—The magnetic susceptibilities were measured by using the Gouy method. All the measurements were calibrated using Hg[Co(NCS)$_4$] as the standard. Diamagnetic corrections for the ligand atoms were computed using a standard source.[10] The susceptibilities were determined at three points in the 78–300°K range. The three temperatures were obtained at liquid nitrogen, Dry Ice–acetone, and room temperatures. A copper–constantan thermocouple connected to a Leeds and Northrup potentiometer was used to measure the temperatures. The accuracy and precision of the measurements were checked with the known susceptibilities of copper(II) acetate monohydrate.[11]

Spectra.—A Perkin-Elmer Model 621 instrument was used for recording the infrared spectra from 4000 to 500 cm^{-1}. Both Nujol mull and KBr disk techniques were employed. Electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. The electronic spectra were recorded from 5000 to 33,300 cm^{-1}.

Results and Discussion

Vanadyl chloride or vanadyl sulfate dihydrate reacts with bivalent tridentate Schiff bases derived from 5-substituted salicylaldehyde or 2-hydroxynaphthaldehyde and 2-aminothiophenol to produce complexes of the type VO(ONS)·nH$_2$O (where n = 0 or 1); ONS represents the tridentate ligand derived from 5-substituted salicylaldehyde or 2-hydroxynaphthaldehyde and 2-aminothiophenol with O, N, and S donor atoms. These tridentate Schiff bases are capable of cyclization if the ligands are heated[12] before reacting with the vanadyl ion. This results in bidentate ligands and a series of oxovanadium(IV) complexes of the type VO(ON)$_2$ can be prepared (where ON represents the bidentate ligand with O and N donor atoms). The analytical data for both of these two series of complexes are presented in Table I. These complexes are greenish yellow and do not melt up to 250°. The complexes are insoluble in water and sparingly soluble in common organic solvents. With the exception of VO(5-Cl-Sal–2-aminothiophenol)-

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TABLE II

INFRARED AND ELECTRONIC ABSORPTION SPECTRAL DATA OF OXOVANADIUM(IV) AND COPPER(II) SCHIFF BASE COMPLEXES[a]

Complex	ν_{max}, cm^{-1}		
	Band I	Band II	ν(V=O), cm^{-1}
VO(5-Cl-Sal–2-aminothiophenol)$_2$	13,700 sh	18,900 sh	900 s
VO(5-NO_2-Sal–2-aminothiophenol)$_2$	13,300 sh	17,100 sh	910 s, 900 s
VO(3-NO_2-Sal–2-aminothiophenol)$_2$	12,750 sh	17,000 sh	920 s
VO(Sal–2-amino-4-chlorothiophenol)$_2$	13,300 sh	18,500 sh	895 s
VO(Sal–2-aminothiophenol)$_2$	14,700 sh	18,200 sh	914 s
VO(5-Cl-Sal–2-aminothiophenol)(H_2O)	13,300 sh		1005 s, 995 s
VO(5-NO_3-Sal–2-aminothiophenol)	14,900 sh		914 s, 904 s
VO(5-Br-Sal–2-aminothiophenol)	18,200 sh		900 s
VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H_2O)	20,000		960 s
Cu(Sal–2-aminothiophenol)	16,100 sh	23,200	
Cu(2-hydroxynaphthaldehyde–2-aminothiophenol)	16,100 sh	22,200	

[a] The electronic spectra were recorded in Nujol mull. Abbreviations: sh, shoulder; s, strong.

(H_2O) and VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H_2O), all other oxovanadium(IV) complexes do not contain any water molecule in their molecular formula. The infrared spectra of these two complexes exhibit a broad water band with medium intensity at about 3400 cm^{-1}. The free water has stretching modes occurring at 3560 and 3520 cm^{-1}; the coordinated water in aquo complexes absorbs[13] at 3095 and 3059 cm^{-1}. The lowering of the water stretching modes to 3400 cm^{-1} in our complexes suggests that the water exists as a coordinated aquo molecule and not simply as water of hydration. Attempts to dehydrate the complexes by heating at 150–160° under vacuum were unsuccessful.

The ν(V=O) stretching frequencies of the complexes are presented in Table II. By comparing the infrared spectra of oxovanadium(IV) complexes with the spectra of the corresponding ligands, the diagnostic V=O stretching frequencies were found in the 895–1005-cm^{-1} region.

As the complexes are sparingly soluble in common solvents, molecular weight measurements were not possible and all electronic spectra were recorded in Nujol mull. The electronic spectral bands are presented in Table II. The VO(5-Cl-Sal–2-aminothiophenol)$_2$ complex and the other complexes of this series exhibit two bands in the 12,000–20,000-cm^{-1} region. These two bands are not well developed and are observed as shoulders. The assignments of electronic spectral bands of oxovanadium(IV) complexes have been a matter of controversy. Recently Vanquickenborne and McGlynn[14] have proposed a new energy level diagram by reconsidering Ballhausen–Gray[15] and Ortolano–Selbin–McGlynn[16] schemes for oxovanadium(IV) complexes. Following this ordering of energy levels (V–M scheme[14]), the first shoulder which is centered at 13,700 cm^{-1} for VO(5-Cl-Sal–2-aminothiophenol)$_2$ is assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition. The second shoulder observed at 18,900 cm^{-1} is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$. The other transition, $d_{xy} \rightarrow d_{z^2}$, is probably covered underneath intraligand and charge-transfer bands. The electronic spectra of the VO(ON)$_2$ complexes are comparable to the spectra of other oxovanadium(IV) complexes reported in the literature.[17]

The electronic spectra of VO(ONS)·$n$$H_2O$ (where n = 0 or 1) are quite different from those of VO(ON)$_2$ complexes. The VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H_2O) complex exhibits one broad but well-developed band at 20,000 cm^{-1}. All other complexes of the VO(ONS)·$n$$H_2O$ series possess one broad absorption band observed as a shoulder in the 13,300–18,200-cm^{-1} region (see Table II). This band is considered to be a d–d transition.

The magnetic susceptibilities and magnetic moments of our complexes are presented in Tables III and IV.

TABLE III

MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF OXOVANADIUM(IV) AND COPPER(II) COMPLEXES AT ROOM TEMPERATURE

Complex	Temp, °K	$10^6\chi_m^{cor}$, cgsu	μ_{eff},[a] BM
VO(Sal–2-aminothiophenol)$_2$	296	1464	1.86
VO(5-Cl-Sal–2-aminothiophenol)$_2$	298	1441	1.86
VO(5-NO_2-Sal–2-aminothiophenol)$_2$	298	1298	1.76
VO(3-NO_2-Sal–2-aminothiophenol)$_2$	298	1194	1.69
VO(Sal–2-amino-4-chlorothiophenol)$_2$	297	1335	1.78
VO(5-Cl-Sal–2-aminothiophenol)(H_2O)	296	698	1.29
VO(5-Br-Sal–2-aminothiophenol)	300	750	1.34
VO(5-NO_2-Sal–2-aminothiophenol)	297	675	1.27
VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H_2O)	297	971	1.52
Cu(Sal–2-aminothiophenol)	297	1410	1.83 (1.82[b])
Cu(2-hydroxynaphthaldehyde–2-aminothiophenol)	298	975	1.53

[a] Calculated using the Curie equation: $\mu_{eff} = (\chi_m^{cor}T)^{1/2}$ BM. No attempt was made to correct the χ_m for temperature-independent paramagnetism. [b] Taken from ref 7 for comparison.

The complexes of the series VO(ON)$_2$ exhibit effective magnetic moments in the range 1.69–1.86 BM. These magnetic moments are very close to the "spin-only" value expected for 3d^1 oxovanadium(IV) complexes with normal magnetic properties.[17] The other series of complexes VO(ONS)·$n$$H_2O$ (n = 0 or 1) exhibit subnormal magnetic moments (μ_{eff} = 1.2–1.5 BM at room temperature). The corrected molar susceptibilities of the VO(ONS)·$n$$H_2O$ complexes range from 675 to 971 cgsu/g-atom of vanadium at room temperature. We studied the susceptibilities of the complexes as a function of temperature in a limited range (at 77, 193, and ~300°K). The magnetic susceptibilities of VO(ONS)·$n$$H_2O$ complexes are dependent on temperature (see Table IV). We observed effective magnetic moments of the complexes in the range 0.93–1.33 BM at 77°K. This temperature dependence of the magnetic susceptibilities indicates the presence of exchange coupled antiferromagnetism in these complexes.[4] A dimeric oxygen-bridged structure, which provides an appro-

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TABLE IV

MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF OXOVANADIUM(IV) AND COPPER(II) COMPLEXES FROM 77 TO 330°K

				193°K		77°K	
Complex	Temp, °K	$10^6\chi_m^{cor}$, cgsu	μ_{eff}, BM	$10^6\chi_m^{cor}$, cgsu	μ_{eff}, BM	$10^6\chi_m^{cor}$, cgsu	μ_{eff}, BM
VO(5-Cl-Sal–2-aminothiophenol)(H_2O)	296	698	1.29	957	1.22	2056	1.13
VO(5-Br-Sal–2-aminothiophenol)	300	750	1.34	1047	1.29	1506	0.96
VO(5-NO_2-Sal–2-aminothiophenol)	297	675	1.27	826	1.13	1405	0.93
VO(2-hydroxynaphthaldehyde–2-aminothiophenol)(H_2O)	297	971	1.52	1444	1.49	2860	1.33
VO(5-Cl-Sal–2-aminothiophenol)$_2$	298	1441	1.86			5391	1.83
Cu(Sal–2-aminothiophenol)	297	1410	1.83	2107	1.81	4563	1.68
Cu(2-hydroxynaphthaldehyde–2-aminothiophenol)	298	975	1.53	1178	1.35	1913	1.09

priate symmetry for the $3d_{xy}$ orbitals of vanadium(IV) to overlap with each other and form a strong σ metal–metal bond, has been suggested for the magnetic abnormality of oxovanadium(IV) complexes of 5-substituted *N*-(2-hydroxyphenyl)salicylidenimine by Zelentsov.[3] This proposed structure has been supported by Ginsberg, *et al.*, from a study of the temperature dependence of the magnetic susceptibilities.[4] The copper(II) complex of the tridentate Schiff base acetylacetone(*o*-hydroxyanil) exhibits a subnormal magnetic moment and has been shown to have a dimeric oxygen-bridged structure from a single-crystal X-ray study.[18] These molecules are however associated in pairs due to a weak bond between the copper atom of one molecule and an oxygen atom of another and are thus weakly tetrameric. The series of VO(ONS)·nH$_2$O complexes are similar to Zelentsov's complexes. It is reasonable, in the absence of structural data, to assume both Zelentsov's complexes and the VO(ONS)·nH$_2$O complexes have a binuclear structure; however, other structures cannot be ruled out. In the binuclear structure the $3d_{xy}$ orbitals of vanadium(IV) have the appropriate symmetry for a σ overlap and this σ metal–metal interaction should be the principal path for spin–spin coupling. Such an interaction leads to a singlet spin state and a higher triplet spin state with an energy separation equal to the exchange integral, J. The magnitude of J and the available thermal energy both make some contribution to the population of the upper triplet state giving rise to magnetic moments of 1.27–1.52 BM at room temperature. We also measured the low-temperature magnetic susceptibilities of the VO(ON)$_2$ complexes. One such example is included in Table IV. The magnetic moments of the VO(ON)$_2$ complexes are independent of temperature and indicate the absence of magnetic exchange in these complexes.

Since oxovanadium(IV) and copper(II) ions resemble each other in having one unpaired electron in their complexes and both form normal and subnormal magnetic moment complexes, we were interested in studying the magnetic properties of analogous copper(II) complexes. Muto reported the magnetic moments of Cu(ONS) complexes to be very close to the "spin-only" value at room temperature.[7] We prepared the complexes Cu(Sal–2-aminothiophenol) and Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) and measured the magnetic moments of these complexes at three temperatures (77, 193, and ~300°K). The complex Cu(Sal–2-aminothiophenol) was found to be so-called "normal" at room temperature and the other complex, Cu(2-hydroxynaphthaldehyde–2-aminothiophenol), exhibited subnormal magnetic property at room temperature. At lower temperatures (see Table IV) the magnetic moment of Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) is lowered considerably indicating the presence of antiferromagnetic exchange. The magnetic moment of Cu(Sal–2-aminothiophenol) is lowered very little (from 1.83 to 1.68 BM at 77°K; see Table IV) in comparison to the 2-hydroxynaphthaldehyde–2-aminothiophenol complex. Proposed structures for tricoordinated copper(II) complexes would be expected to lead to subnormal magnetic properties and we believe Cu(Sal–2-aminothiophenol) is involved in weak magnetic exchange. Presumably electronic effects are responsible for greater magnetic exchange in the Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) complex in comparison to Cu(Sal–2-aminothiophenol). Although a room-temperature magnetic moment of 1.83 BM is very close to the spin-only value for copper(II), this may be considered as a lowered value from an original value of 2.1–2.2 BM calculated for tetragonal copper(II) complexes.[19]

From the comparison of magnetic properties of these oxovanadium(IV) and copper(II) complexes it is apparent that the phenomenon of antiferromagnetism exists in lesser degrees in copper(II) complexes as compared to the corresponding oxovanadium(IV) complexes. The symmetries of the unpaired electrons in these two metal ions are quite different. In copper(II) complexes, the unpaired electron is in the $d_{x^2-y^2}$ orbital and electronic spin–spin coupling takes place by superexchange through the bridging atoms in tridentate ligands.[20] In case of oxovanadium(IV), the unpaired electron is in the d_{xy} orbital and the overlap of d_{xy} orbitals of adjacent vanadium atoms leads to direct spin–spin coupling with stronger V–V interaction.

After completion of this work, our attention was drawn to a recent publication[21] concerning the magnetic properties of the copper(II) complexes reported in this study. They reported Cu(Sal–2-aminothiophenol) to have magnetic moments 1.76–1.81 BM as a function of temperature. The temperature variations deviate slightly from simple Curie–Weiss behavior and weak magnetic exchange has been proposed. The Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) has been reported to have moments of 0.90–1.54 BM as a function of temperature. Thus our magnetic data are in close agreement with their results.

We have also recorded the electronic spectra of Cu(Sal–2-aminothiophenol) and Cu(2-hydroxynaphthaldehyde–2-aminothiophenol). Since these complexes are insoluble in common aqueous and nonaqueous solvents, only Nujol-mulled spectra were recorded. The electronic spectral bands are included in Table II. Both

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complexes exhibit a well-developed band around 23,000 cm^{-1} (band II) and a broad shoulder centered around 15,800 cm^{-1} (band I). Band I can be safely identified with d–d transitions of the copper(II). In the absence of molar extinction coefficient data, it is difficult to assign band II. It is interesting to note that the electronic spectra of these two complexes are very similar and almost superimposable on each other. One may conclude that if Cu(2-hydroxynaphthaldehyde–2-aminothiophenol) is involved in magnetic exchange, the other complex should also exhibit the same phenomenon. This conclusion has also been supported from the magnetic data.

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The Oxidation of Bis(π-cyclopentadienyldicarbonyliron) by Anhydrous Ferric Perchlorate in Acetone. A General Route to Complexes of the Types (π-C_5H_5)Fe(CO)$_2$X and (π-C_5H_5)Fe(CO)$_2$L$^+$ [1]

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[(π-C_5H_5)Fe(CO)$_2$]$_2$ is oxidized by 2 mol of Fe(III) in acetonitrile or acetone to give the solvent-bound complexes (π-C_5H_5)Fe(CO)$_2$NCCH$_3$$^+$ and (π-C_5H_5)Fe(CO)$_2$OC(CH$_3$)$_2$$^+$. The coordinated acetone in the latter is easily displaced by a variety of ligands giving the complexes (π-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I, NCS, SCN, ONO$_2$) and (π-C_5H_5)Fe(CO)$_2$L$^+$ (L = py, P(C_6H_5)$_3$, CO, S(C_2H_5)$_2$).

We wish to report details of a simple and general route to complexes of the types (π-C_5H_5)Fe(CO)$_2$X and (π-C_5H_5)Fe(CO)$_2$L$^+$ from bis(π-cyclopentadienyldicarbonyliron).[3] Various methods have previously been used for the preparation of such compounds: (i) Direct reaction of [(π-C_5H_5)Fe(CO)$_2$]$_2$ with halogens gives, for example, (π-C_5H_5)Fe(CO)$_2$I.[4] (ii) Oxidative fission of the metal–metal bond in [(π-C_5H_5)Fe(CO)$_2$]$_2$ by oxygen in the presence of coordinating anions gives, for example, (π-C_5H_5)Fe(CO)$_2$SCN and (π-C_5H_5)Fe(CO)$_2$NCS.[5] (iii) Reduction of [(π-C_5H_5)Fe(CO)$_2$]$_2$ by sodium amalgam, followed by reaction of the anion, without isolation, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$S(CH$_3$)$_2$$^+$.[6] (iv) Isolation of ($\pi$-$C_5H_5$)Fe(CO)$_2$Cl or ($\pi$-$C_5H_5$)Fe(CO)$_2$Br, followed by displacement of the halide ion, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$OCOCF$_3$[7] and (π-C_5H_5)Fe(CO)$_2$P(C_6H_5)$_3$$^+$.[8] In the latter case, (π-C_5H_5)Fe(CO)P(C_6H_5)$_3$Cl is also a product. (v) Isolation of (π-C_5H_5)Fe(CO)$_2$Cl followed by treatment with a neutral ligand in the presence of a halogen acceptor, such as aluminum trichloride, gives, *e.g.*, (π-C_5H_5)Fe(CO)$_2$(NH$_2$NH$_2$)$^+$,[9] (π-C_5H_5)Fe(CO)$_2$NCCH$_3$$^+$,[10] and ($\pi$-$C_5H_5$)Fe(CO)$_3$$^+$.[8] (vi) Isolation of ($\pi$-$C_5H_5$)Fe(CO)$_2$Cl, conversion to ($\pi$-$C_5H_5$)Fe(CO)$_3$$^+$, and treatment with pyridines gives (π-C_5H_5)Fe(CO)$_2$py$^+$,[10] and with azide ion gives (π-C_5H_5)Fe(CO)$_2$NCO.[11] Many of these preparations require anaerobic conditions, anhydrous solvents and atmospheres, extended reaction times, and special apparatus.

Oxidation of metal carbonyl compounds using transition metal oxidants, such as FeCl$_3$ or Ce(IV), often leads to degradation of the complex. For example, *trans,trans,trans*-1-phenyl-6-*p*-tolyl-1,3,5-hexatriene is produced by treatment of the hexatrieneiron tricarbonyl complex with ferric chloride in acetonitrile,[12] and cyclobutadiene is a transient intermediate in the decomposition of cyclobutadieneiron tricarbonyl by ceric ion.[13] However, in other cases simple oxidation products are obtained. Ferric chloride oxidation of Cr(CO)$_5$I$^-$ in acetic acid gives the chromium(I) complex Cr(CO)$_5$I,[14] and the same oxidant converts Co$_6$(CO)$_{15}$$^{2-}$ into Co$_6$(CO)$_{16}$.[15]

We find that [(π-C_5H_5)Fe(CO)$_2$]$_2$ is rapidly and quantitatively oxidized in a variety of solvents by Fe(III) (either as Fe(ClO$_4$)$_3$ or Fe(OH$_2$)$_6$Cl$_3$). In strongly coordinating solvents, the solvent-bound complex formed in the oxidation is readily isolated; for example, from acetonitrile we isolate (π-C_5H_5)Fe(CO)$_2$NCCH$_3$$^+$. In the weakly coordinating solvent acetone, the initial product of oxidation is the solvento complex (π-C_5H_5)Fe(CO)$_2$(OC(CH$_3$)$_2$)$^+$. The weakly bound solvent molecule is easily displaced by a variety of neutral and anionic ligands to give the complexes (π-C_5H_5)Fe(CO)$_2$L$^+$ (L = neutral ligand) and (π-C_5H_5)Fe(CO)$_2$X (X = anionic

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