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

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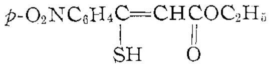
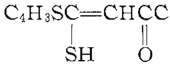
In a previous paper[1] three monomeric monothio-β-diketone (mtdk) complexes of VO^{2+} were reported which had properties consistent with square-pyramidal structures. Livingstone and coworkers,[2] on the other hand, have reported that a dimeric complex is formed from the fluorinated monothio-β-diketone 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



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

Hnebas



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

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 $NaC_2H_3O_2 \cdot 3H_2O$ 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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idine, the complexes dissolve readily; however, even in this solvent the complexes decompose to brown or black insoluble materials within a period of approximately 1 hr, and it has not been possible to isolate the pyridine adducts as solids. The decomposition products have not been identified. Magnetic and optical data are given in Table I.

TABLE I

MAGNETIC AND OPTICAL DATA

Medium	g_0	$\Delta H_{4,5}$, G	$\mu_{\text{eff}}^{\text{cor}}$, BM	$E_{\max}$, kK
		VO(ttmbs)$_2$		
Solid	1.972^a		1.78	22.2,^{c} 15.4,^{b,c} 12.4
Pyridine	1.975	93		23.8, 15.6, 13.0^c
Methylene chloride	1.974	99		24.7, 18.2,^{c} 13.0^b
		VO(nebas)$_2$		
Solid	1.974^a		1.70	26.0, 17.0,^{c} 12.2
Pyridine	1.975	92		29.4,^{c} 16.1,^{c} 13.2
Methylene chloride	1.976	98		28.2,^{c} 17.3

[a] Measured for powdered solid. No hyperfine interaction observable. [b] Very weak, broad, and poorly defined. [c] Shoulder.

Results and Discussion

That the complexes derived from Hnebas and Httmbs do not have structures in the solid state analogous to that of the three green monothio-β-diketones reported previously[1] (VO(bas)$_2$, VO(dbms)$_2$, and VO(ebas)$_2$) is suggested by their gold color. Further, the molecular weight results reported by Livingstone[2] indicate that VO(ttmbs)$_2$ should not be formulated as a monomer.

Infrared spectral measurements on the complexes derived from Httmbs and Hnebas also indicate that these compounds differ structurally from the green series of compounds. As reported previously VO(bas)$_2$, VO(dbms)$_2$, and VO(ebas)$_2$ exhibit a characteristic V=O stretching frequency in the range 980–995 cm^{-1}. An analogous band is not found in the infrared spectra of VO(ttmbs)$_2$ and VO(nebas)$_2$ and, in fact, in the latter compound there are no bands of significant intensity in the 900–1000-cm^{-1} region. In VO(ttmbs)$_2$ bands of moderate intensity are observed at 926 and 946 cm^{-1}; however, these bands are reasonably assigned as ligand absorptions, since similar bands are found at 920 and 929 cm^{-1} in Httmbs itself (Figure 1). Furthermore, it can be pointed out that the bands at 926 and 946 cm^{-1} in VO(ttmbs)$_2$ remain unshifted in the pyridine adduct of this complex (*vide infra*).

As can be seen in Figure 1, VO(ttmbs)$_2$ exhibits a strong, sharp band at 868 cm^{-1} that cannot reasonably be assigned as a ligand absorption. A similar band is found at 876 cm^{-1} in VO(nebas)$_2$. We assign these bands as V=O stretching frequencies. This assignment places the V=O stretching frequencies in the gold compounds some 100 cm^{-1} lower than is normally observed[7] in vanadyl(IV) complexes. Recently a similar lowering of the V=O stretching frequency (854 cm^{-1}) was observed in the Schiff base complex *N,N'*-propylenebis(salicylaldiminato)oxovanadium(IV), VO(salpn)$_2$.[8] In an X-ray crystallographic study it was then shown that VO(salpn)$_2$ consists of infinite chains of molecules packed so that the vanadyl oxygen atom of one molecule occupies the sixth coordination position about the V atom in a neighboring molecule. It was further suggested that a low ν(V=O) frequency may be a good indication of oxygen bridging in vanadyl(IV) complexes. Very recently Farmer and Urbach[9] have reported that the VO^{2+} complex derived from a similar Schiff base, VO(sal)$_2$-(+)tnCH$_3$, exhibits in the solid state an unusually low V=O stretching frequency of 855 cm^{-1}. This observation was interpreted in terms of bridging vanadyl groups. Thus we are led to believe by the infrared results that the solid-state structures of VO(ttmbs)$_2$ and VO(nebas)$_2$ also involve –V–O–V– bridging.

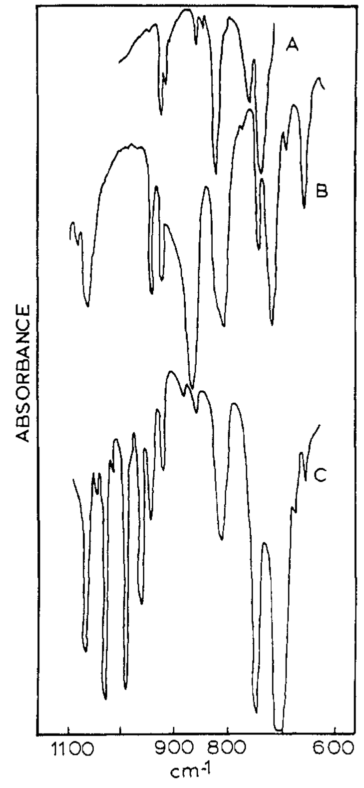

Figure 1.—Infrared spectra of Httmbs (A), VO(ttmbs)$_2$ (B), and VO(ttmbs)$_2$py (C).

Since it is thought that the previously reported mtdk complexes become six-coordinate in coordinating solvents,[1] in common with many other VO^{2+} compounds, we have investigated the behavior of VO(ttmbs)$_2$ and VO(nebas)$_2$ in pyridine. As can be seen in Figure 1 treatment of VO(ttmbs)$_2$ with pyridine results in the disappearance of the band at 868 cm^{-1} and the appearance of a strong, new band at 964 cm^{-1}. The new band cannot be assigned as a pyridine absorption, although bands characteristic of pyridine are present in the spectrum at 990 and 1030 cm^{-1}, as well as at other frequencies.[10,11] Similar results were obtained when VO(nebas)$_2$ was treated with pyridine; a new band appeared at 969 cm^{-1}, while the 876-cm^{-1} band disappeared. The position of these new bands is very similar to that of the bands assigned as the V=O stretching frequencies in the pyridine adducts of the previously reported VO(mtdk)$_2$ complexes. These results suggest that pyridine successfully competes with the oxygen atoms for the sixth coordination position on the vanadium atoms, with concomitant

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destruction of the –V–O–V– bridging system and the formation of monomers.

In view of the apparent structure of the compounds reported here, it was of interest to determine their molecular weights. This work was frustrated by the low solubility of the compounds in suitable solvents. Livingstone and coworkers[2] formulated VO(ttmbs)$_2$ as a dimer, based on a cryosopically determined molecular weight of 910 (calculated for dimer 1082) in nitrobenzene; however, the low solubility of VO(ttmbs)$_2$ in nitrobenzene suggests that this figure may be subject to considerable error. By using a vapor pressure osmometer we have obtained values ranging from 720 to 810 in methylene chloride as the solvent. Again the solubility is such that the results are of questionable accuracy. For VO(nebas)$_2$ we have obtained values that are close to that calculated for the monomer. This suggests that even in noncoordinating solvents the –V–O–V– bridging is disrupted upon dissolution with the formation of either monomers or an equilibrium mixture of monomers and more highly bridged species. This same type of phenomenon was also observed in the case of VO(sal)$_2$(+)tnCH$_3$, where the V=O stretching frequency was observed at 991 cm^{-1} in chloroform solutions.[9]

The magnetic moments of the subject complexes at room temperature compare with the spin-only value and the solution esr parameters are similar to those that we have reported previously for VO(mtdk)$_2$ complexes. Optical spectra of VO(ttmbs)$_2$ are shown in Figure 2. Similar spectra were exhibited by VO(nebas)$_2$, as indicated in Table I. The diffuse reflectance spectra differ considerably from those observed for the previously reported square-pyramidal compounds, again emphasizing the structural differences in the solid state. Solutions of both VO(ttmbs)$_2$ and VO(nebas)$_2$ in pyridine exhibit electronic spectral properties which are essentially identical with those previously reported for the square-pyramidal VO(mtdk)$_2$ complexes dissolved in pyridine. Again this observation is consistent with the notion that the solid-state bridged structure is broken down by strong donor solvents with the concomitant formation of monomeric pyridine adducts.

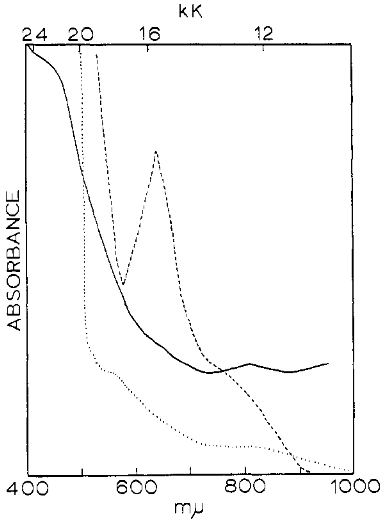

Figure 2.—Optical spectra of VO(ttmbs)$_2$: ——, diffuse reflectance; – – –, pyridine; · · · ·, methylene chloride.

The most obvious difference between the ligands that form monomeric complexes and those that give rise to extended structures is that the latter ligands have electron-withdrawing groups present. In VO(ttmbs)$_2$ and VO(nebas)$_2$ the electron density on the vanadium atoms may be reduced by the electron-withdrawing groups to such an extent that the increased Lewis acidity of the vanadium atoms makes –V–O–V– bridging possible.

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Complexes of Maleonitriledithiolate with Metals of Group III

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Complexes of transition metals with ligands containing the *cis*-1,2-enedithiol structural unit[1] have been the subject of numerous studies in the past 10 years. The field has been reviewed several times.[2]

A few reports of complexes of dithiolene ligands with posttransition metals have appeared.[3] Tuck and coworkers[3c,4] have described salts of the anions In(mnt)$_2^-$ and In(mnt)$_3^{3-}$, where mnt^{2-} is the ligand maleonitriledithiolate, *cis*-1,2-S$_2$C$_2$(CN)$_2^{2-}$. They also have reported briefly the results of a crystal structure study of the six-coordinate tris complex.[3c] We wish now to present results which supplement and extend those of Tuck and coworkers.

Reaction of the sodium salt of the ligand with thallium(III) chloride in a ratio of 3:1 or greater gave salts of the six-coordinate tris complex ion Tl(mnt)$_3^{3-}$. Similarly, reaction of Na$_2$mnt with indium(III) chloride in a 3:1 ratio led to salts of the previously reported[3c,4] complex ion In(mnt)$_3^{3-}$. It was found that salts of Tl(mnt)$_3^{3-}$ also could be prepared more conveniently by reaction of thallium(I) bromide or acetate with an excess of Na$_2$mnt in the presence of atmospheric oxygen.

When the ratio of reactants was 2:1, reaction of mnt^{2-} with tetrabromothallate yielded products having the composition Q$_2$Tl(mnt)$_2$Br, where Q is a quaternary ammonium cation. From the analogous reaction

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