

Biscyclopentadienylniobium Complexes Containing the Molecular Unit S₂ as a Ligand

P. M. Treichel and G. P. Werber

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Abstract: The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and H_2S in methanol, in the presence of an ionic halide or pseudohalide (KCl, KBr, NH_4I , KSCN), gives the red to violet monomeric complexes $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$). These complexes contain the molecular unit S_2 as a ligand, and as such are analogous to oxygen complexes which have been described recently. In two of these reactions ($\text{X} = \text{Cl}, \text{Br}$) a second compound having the same formula was obtained; these compounds are believed to be polymeric, with disulfide bridging groups between metal atoms. If H_2S and $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ are allowed to be in contact for a prolonged period, another polymeric species, $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_4]_n$, is formed. Methyl iodide and $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$ react to give CH_3SSCH_3 and $(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2\text{Cl}$. In this reaction a second compound $(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$ was also found.

Few biscyclopentadienylniobium complexes have been described. The best characterized of these compounds are of the formula $(\pi\text{-C}_5\text{H}_5)_2\text{NbX}_3$ or $(\pi\text{-C}_5\text{H}_5)_2\text{NbX}_2\text{OH}$ ($\text{X} = \text{Br}, \text{Cl}$).¹ The later reference² includes a report of several niobium(IV) complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{NbX}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{NbXOH}$ ($\text{X} = \text{Cl}, \text{Br}$), although these compounds are not well characterized. There is also a report of a compound $(\pi\text{-C}_5\text{H}_5)_2\text{NbClBH}_4$.³

We undertook a study of biscyclopentadienylniobium (and -tantalum) chemistry, anticipating that we would find some striking differences between compounds of these elements and those of the first transition element in this group, vanadium. That such differences would be found is suggested by the existence of well-characterized complexes of niobium(V) only whereas biscyclopentadienyl complexes of vanadium(II) $(\pi\text{-C}_5\text{H}_5)_2\text{V}$,⁴ vanadium(III) $(\pi\text{-C}_5\text{H}_5)_2\text{VX}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{V}^+$,⁵ and vanadium(IV) $(\pi\text{-C}_5\text{H}_5)_2\text{VX}_2$ ¹ have been made.^{6,7} Herein we report the unexpected synthesis of several niobium complexes of the formula $(\pi\text{-C}_5\text{H}_5)_2\text{Nb(L)X}$, where L is the two-electron donor ligand S_2 . These complexes were formed in the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and H_2S . Several other niobium complexes are also reported here including $(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$, $(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2\text{Cl}$, and $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{X}]_n$. The last is a second product of the $\text{H}_2\text{S}-(\pi\text{-C}_5\text{H}_5)_2\text{NbX}_2\text{OH}$ reaction ($\text{X} = \text{Cl}, \text{Br}$).

Experimental Section

Infrared spectra were recorded on a Beckman IR-10 grating spectrophotometer using Nujol mulls. Ultraviolet spectra were run on a Cary-14 recording spectrophotometer. These data are listed in Tables I and II. Proton nmr measurements were made on a Varian HA-100 spectrometer at 100 Mc. Mass spectral data were obtained on a Consolidated Electrodynamics Corp. Type 21-103C mass spectrometer.

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Microanalyses were performed by A. Bernhardt Microanalytical Laboratory, Mülheim, Germany, and Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weight determinations were made osmometrically by the Galbraith Laboratories.

Table I. Infrared Spectra of Biscyclopentadienylniobium Compounds (cm^{-1})

$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$	3090 m, br, 1445 s, 1430 s, 1125 vw, 1065 w, 1020 m, 1005 m, 960 vw, 925 vw, 875 sh, 845 s, 820 s, 720 vw, 595 vw, 540 m, 355 w
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$	3110 m, 3080 m, 1430 m, 1070 w, 1040 w, sh, 1010 s, br, 890 w, 835 s, br, 590 vw, 520 m, 340 w
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}$	3100 w, 3080 w, 1140 s, 1428 m, 1123 vs, 1063 w, 1020 m, 1003 m, 843 s, 820 s, 715 vw, 540 m
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{I}$	3090 w, 1435 s, br, 1120 vw, 1070 w, 1017 m, 1005 m, 825 s, br, 870 m, sh, 855 s, 830 m, sh, 810 s, 590 vw, 540 m
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{SCN}$	3090 w, 2060 s, br, 1440 m, br, 1120 vw, 1065 vw, 1020 m, sh, 1005 m, 825 s, br, 540 m, 350 w
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{CN}]_n$	3090 w, 2040 s, br, 1440 m, br, 1120 vw, 1065 sh, 1010 s, br, 820-850 s, br, 525 m, 345 w
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_4]_n$	3090 w, br, 1435 m, 1160 vw, 1120 vw, 1060 w, 1010 m, 820 m, br, 675 m, 665 m, sh, 540 w, 520 w
$(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2\text{Cl}$	3050 w, br, 1430 m, 1120 vw, 1060 vw, 1015 sh, 1005 m, 847 s, 725 s, br, 575 w, 375 vw
$(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$	3100 s, 1425 m, 1360 m, 1120 vw, 1055 vw, 1020 m, 998 m, 935 vw, 860 s, 848 s, 815 s, 755 vw, 595 vw, 348 m

Biscyclopentadienylniobium dichloride hydroxide was prepared by the procedure described by Wilkinson and Birmingham¹ for synthesis of $(\pi\text{-C}_5\text{H}_5)_2\text{NbBr}_2\text{OH}$, except that the crude mixture resulting from addition of sodium cyclopentadienide to niobium pentachloride in tetrahydrofuran was intentionally hydrolyzed by the addition of water so that all $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_3$ was converted to this product.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$. A solution of 1.000 g (3.215 mmoles) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and 0.442 g (3.215 mmoles) of KCl in 250 ml of methanol and 150 ml of benzene was prepared. Hydrogen sulfide was bubbled through the solution with mild agitation for periods of 2 min at 0, 0.75-, and 3-hr intervals during the total reaction time of 4 hr, keeping the reaction flask stoppered between additions.

The color of the solution slowly changed from yellow to red during this period, and, after the reaction was complete, the total

volume was reduced to ~150 ml by evaporating the solvents under vacuum. Several 100-ml portions of toluene were added to the concentrated solution; following each addition 100 ml of solvent was removed under vacuum. Usually after the third addition of toluene a gray-green precipitate was formed, removed by filtra-

Table II. Ultraviolet Data for Biscyclopentadienylniobium Compounds^a

Compound	Absorption, Å	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$	4820	8.99×10^3
	3680	9.15×10^3
	2720	7.75×10^3
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$	4590	9.25×10^3
	3430	4.58×10^3
	3000 sh	8.02×10^3
	2660	9.96×10^3
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}$	4750	1.147×10^3
	3720	1.152×10^3
	2860 sh	8.30×10^4
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{I}$	4700	8.37×10^3
	3720	3.085×10^3
	2900	6.84×10^3
$(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{SCN}$	4500	9.20×10^3
	4130	3.95×10^3
	2540	1.04×10^4
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{CN}]_n$	4420	9.65×10^2
	3380 sh	4.22×10^3
	3000 sh	9.20×10^3
	2650	1.26×10^4
$[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{I}]_n$	3330	9.00×10^3
$(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$	2530	1.02×10^4

^a Solution in ethanol.

tion, and discarded. The remaining solvent was removed by evaporation under vacuum leaving a dry, dark red material. This crude product was dissolved in 500 ml of benzene and filtered and the solvent removed by evaporation under vacuum. The product was chromatographed on a silica gel column using a solution of two parts benzene and one part acetone as eluent. The column must be prepared with the same solution. Two bands developed on the column. The first to elute was a red band which was found to contain the monomeric $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$. This compound was isolated by evaporating the solvent and washing the purplish product with two 5-ml portions of benzene. The second band to elute was a yellow band which was removed from the column using a solution of one part acetone and one part benzene as eluent. The solvent was removed under vacuum and the yellow-orange polymeric $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$ washed with two 10-ml portions of petroleum ether (bp 60–68°). The products were further purified by rechromatographing them and repeating the washings. The yield of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$ was 0.24 g, 23%, mp 225° dec.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}_2\text{NbCl}$: C, 37.22; H, 3.13; S, 19.87; Nb, 28.79; Cl, 10.99; mol wt, 323. Found: C, 37.78; H, 3.36; S, 19.16; Nb, 30.26; Cl, 10.23; mol wt, 350.

The yield of $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$ was 0.031 g, 3.0%, mp 150° dec.

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}_2\text{NbCl}$: C, 37.22; H, 3.13; S, 19.87; Nb, 28.79; Cl, 10.99. Found: C, 37.12; H, 3.20; S, 19.65; Nb, 28.14; Cl, 10.96.

The red monomer can be partially converted to the orange polymer by dissolving 0.1 g of the former material in 25 ml of dichloromethane, adding 100 ml of petroleum ether (bp 90–100°), and slowly heating the solution on a steam bath to 65°. The remaining solvent is removed under vacuum and the solid chromatographed as described previously.

The proton nmr spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$ showed a single sharp resonance at τ 4.01. The presumed polymeric material showed two resonances of unequal intensities at τ 4.03 and 4.09.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}]_n$. The reaction of 1.000 g (3.215 mmoles) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and 0.765 g (6.43 mmoles) of KBr in 500 ml of methanol was run in a manner similar to that described for the preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$. The solvent was removed by evaporation, the product dissolved in 200 ml of dichloromethane, and the solution filtered. The solvent was removed under vacuum and the crude product chromatographed three times using a silica gel column prepared with a solution of 20% acetone and 80% benzene and eluted with this same solvent mixture. Two bands were obtained. The first to elute was the dark red crystalline product, and the second band contained a very small amount of a light orange material which was not analyzed but was presumed to be the polymeric $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}]_n$. The dark red crystalline monomer was obtained on evaporation of the solvent under vacuum; it was washed with three 10-ml portions of 60–68° petroleum ether (0.066 g, 5.6% yield, mp 225° dec).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}_2\text{NbBr}$: C, 32.17; H, 2.75; S, 17.47; Nb, 25.31; Br, 21.76. Found: C, 32.29; H, 2.61; S, 16.98; Nb, 25.80; Br, 21.17.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{I}$. This compound was prepared in a manner analogous to the preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$, using 0.500 g (1.61 mmoles) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and 0.466 g (3.215 mmoles) of NH_4I in 250 ml of methanol. The product was chromatographed twice using one part acetone and two parts benzene as the eluent. Only one band was eluted. The solvent was evaporated under vacuum and the dark purple crystalline product was washed with three 10-ml portions of 60–68° petroleum ether (0.2871 g, 43% yield, mp 230° dec).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}_2\text{NbI}$: C, 29.00; H, 2.44; S, 15.50; Nb, 22.40; I, 30.50. Found: C, 29.20; H, 2.48; S, 15.47; Nb, 22.38; I, 30.46.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{SCN}$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{NbSSCN}]_n$. This compound was prepared in a manner analogous to the preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Br}$ using 1.000 g (3.215 mmoles) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and 0.624 g (6.43 mmoles) of KSCN in 300 ml of methanol. The solution turned red upon the addition of the KSCN, yellow again shortly after the introduction of the gas. The crude product was chromatographed on a silica gel column using a solution of one part acetone and two parts benzene as eluent. Two bands were seen to elute. The first, a red band contained the monomeric $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{SCN}$. The second, a yellow band containing $[(\pi\text{-C}_5\text{H}_5)_2\text{NbSSCN}]_n$, was eluted with a solution of one part acetone and one part benzene. The solvent was removed by vacuum and each product chromatographed two more times. The brown crystalline monomeric compound and the yellow amorphous polymeric material were each washed with three 5-ml portions of 60–68° petroleum ether. The yield of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{SCN}$ was 0.204 g, 18%, mp 230° dec.

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{S}_2\text{NbN}$: C, 38.26; H, 2.92; S, 27.86; Nb, 26.90; N, 4.05. Found: C, 38.50; H, 2.98; S, 27.29; Nb, 27.19; N, 4.20.

The yield of $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{CN}]_n$ was 0.11 g, 11%, mp 134° dec.

Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{S}_2\text{NbN}$: C, 42.17; H, 3.22; S, 20.47; Nb, 29.66; N, 4.47. Found: C, 41.73; H, 3.66; S, 19.91; Nb, 27.90; N, 3.73. C_5H_5 proton nmr resonances were noted at τ 4.02 and 4.07.

Preparation of $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_4]_n$. A solution of 2.00 g (6.430 mmoles) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2\text{OH}$ and 0.884 g (6.430 mmoles) of KCl in 500 ml of methanol was prepared. Hydrogen sulfide was introduced in the usual manner and the solution allowed to remain stoppered for 2 days during which time a brown precipitate formed. The precipitate was removed by filtration and washed twice with 300-ml portions of methanol and once with 100 ml of benzene, allowing a 3-hr contact time during each washing. The crude material was dried and the pure product extracted with and crystallized from carbon disulfide and then washed with a 5-ml portion of dichloromethane (0.094 g, 4.2% yield).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}_4\text{Nb}$: C, 34.19; H, 2.85; S, 36.47; Nb, 26.50. Found: C, 34.57; H, 2.95; S, 36.51; Nb, 26.45.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2\text{Cl}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$. A 5-ml portion of CH_3I was added to a solution of 0.100 g (0.310 mmole) of $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}$ in 25 ml of dichloromethane, and the reactants were allowed to remain in a stoppered 50-ml round-bottom flask for 24 hr. At that time the odor of methyl disulfide was much in evidence. A dark red crystalline material precipitated from the dark red solution leaving a light straw yellow solution which was separated from the crystals by filtration. The dark crystals of

($\pi\text{-C}_5\text{H}_5$)₂NbI₂Cl were washed with 25 ml of benzene and 25 ml of 60–68° petroleum ether and dried (0.0573 g, 36% yield, mp 145° dec).

Anal. Calcd for C₁₀H₁₀I₂CINb: C, 23.43; H, 1.97; I, 49.54; Cl, 6.92; Nb, 18.13. Found: C, 22.19; H, 2.16; I, 49.70; Cl, 7.30; Nb, 18.35.

The presence of methyl disulfide in the original solution was subsequently confirmed by vpc, by comparison of its retention time with known samples in dichloromethane. An approximate value of the amount of methyl disulfide (~60%) was also ascertained.

A 200-ml portion of benzene was added to the remaining filtrate and the volume reduced to ~100 ml, precipitating a small amount of a dark yellow material which was removed by filtration and discarded. A 200-ml portion of heptane was added to the remaining filtrate and poured in a 500-ml round-bottom flask and the solvent removed under vacuum. The product was extracted twice with 500 ml of hot 60–68° petroleum ether and precipitated from the ether as long white fibrous crystals (0.0126 g, 14.8% yield, mp 192° dec).

Anal. Calcd for C₁₀H₁₀NbOCl: C, 43.74; H, 3.68; Nb, 33.84; Cl, 12.91; mol wt, 274.6. Found: C, 43.08; H, 3.54; Nb, 34.10; Cl, 13.64; mol wt, 264. The parent peak in the mass spectrum was at 274; the C₅H₅ proton nmr resonance was noted at τ 3.65.

This compound can also be prepared in about the same yields by adding 0.1000 g of ($\pi\text{-C}_5\text{H}_5$)₂NbI₂Cl to a solution of 500 ml of 90–100° petroleum ether, 30 ml of dichloromethane, and 5 ml of CH₃I. The contents are warmed to ~35° and stirred for 24 hr. Most of the starting material did not dissolve and was removed from the violet solution by filtration. The solvent was removed by filtration and the white product crystallized from the solution by removing the solvent under vacuum. The solvent stripped from the above filtrate also had the violet color suggesting the presence of iodine.

Discussion

The monomeric compounds ($\pi\text{-C}_5\text{H}_5$)₂NbS₂X (X = Cl, Br, I, SCN) were characterized initially by analyses and molecular weight. They are diamagnetic since the C₅H₅ ring protons showed a sharp nmr resonance in the expected position. The infrared spectra of these complexes showed bands associated with biscyclopentadienylmetal systems.⁸

We were concerned initially that these compounds might have the formula ($\pi\text{-C}_5\text{H}_5$)₂Nb(SH)₂X rather than the reported one. These two possible stoichiometries could not be differentiated by the above information, and moreover the niobium–thiol formulation would be closely analogous to the known complex ($\pi\text{-C}_5\text{H}_5$)₂Ti(SH)₂,⁹ and similar to many other mercaptometal complexes such as ($\pi\text{-C}_5\text{H}_5$)₂Ti(SR)₂^{10,11} and ($\pi\text{-C}_5\text{H}_5$)₂Zr(SR)₂¹² which have been reported. However, the lack of a band in the infrared spectra of these compounds at about 2500 cm⁻¹ which would be expected for $\nu_{\text{S-H}}$, and also the lack of a proton resonance at about τ 6.5, in the region expected for a thiol proton, convinced us of the ($\pi\text{-C}_5\text{H}_5$)₂NbS₂X formulation. Subsequently preliminary results from an X-ray crystallographic study have confirmed our formulation.¹³

These organometallic compounds may thus be regarded as metal complexes of the molecular unit S₂.¹⁴

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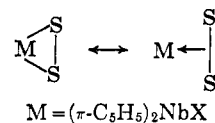
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(14) Several compounds with bridging S₂ groups are known including [SfFe(CO)₃]₂ (W. Hieber and J. Gruber, *Z. Anorg. Allgem. Chem.*, **296**, 91 (1958); C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965)) and [NbS₂Br]₂ and [NbS₂Cl]₂ (H. Schäfer, D. Bauer, W. Beckmann, R. Gerken, H. G. Nieder-Vahrenholz, K. J. Niehuis, and H. Scholtz, *Naturwissenschaften*, **51**, 241 (1964)).

By analogy to the structure reported for the oxygen complexes Ir[(C₆H₅)₃P]₂(CO)X·O₂ (X = Cl,¹⁵ I¹⁶) one would predict a geometry in which the metal and two sulfur atoms make up a three-membered ring. The bonding, in valence bond terms, would be



The infrared spectrum of these complexes is in accord with an over-all structure involving canted cyclopentadienyl rings such as has been found for ($\pi\text{-C}_5\text{H}_5$)₂MoH₂,¹⁷ ($\pi\text{-C}_5\text{H}_5$)₂TiCl₂Al(C₂H₅)₂,¹⁸ and ($\pi\text{-C}_5\text{H}_5$)₂Ti(SC₆H₅)₂.¹⁹ Thus in each compound one sees a characteristic doublet of about medium intensity a little above 1000 cm⁻¹ and also two strong bands around 820–860 cm⁻¹, which are associated with the C₅H₅ ring deformations in compounds having this geometry. A band at about 540 cm⁻¹ is seen in all of these complexes and is probably associated with $\nu_{\text{S-S}}$.

The novelty of these complexes is heightened, of course, by the fact that the free S₂ molecule does not exist at room temperature.²⁰ Diatomic sulfur, S₂, is known to be present in gaseous sulfur at high temperatures, but it is unstable with respect to aggregation at room temperature. Coordination to a transition metal has allowed this substance to be stabilized in these complexes.

The reaction of ($\pi\text{-C}_5\text{H}_5$)₂NbS₂Cl and CH₃I to give CH₃SSCH₃ and ($\pi\text{-C}_5\text{H}_5$)₂NbS₂Cl further confirms the given formula and in addition gives a useful synthetic route to mixed halides of the formula ($\pi\text{-C}_5\text{H}_5$)₂NbX₂Y. From this reaction a second compound was also obtained as white needles. This compound had the formula ($\pi\text{-C}_5\text{H}_5$)₂NbOCl. We are uncertain as yet as to its origin in this reaction.

In the synthesis of ($\pi\text{-C}_5\text{H}_5$)₂NbS₂X (X = Cl, Br), a second diamagnetic compound having the same formula was obtained. It could be separated by chromatography on a silica gel column using a polar solvent (acetone), with the monomer eluting first. These compounds are believed to be polymeric by virtue of their insolubility, but no molecular weights could be obtained. A polymeric formulation involving disulfide bridging groups is reasonable, and these compounds could then be regarded as analogous to ($\pi\text{-C}_5\text{H}_5$)₂NbX₂Y systems where X in this case is the disulfide bridge.

In the preparation of ($\pi\text{-C}_5\text{H}_5$)₂NbS₂SCN, a second polymeric species was also obtained. Surprisingly,

(15) S. J. La Placa and J. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(16) S. J. La Placa and J. Ibers, *Science*, **155**, 740 (1967).

(17) M. Gerlach and R. Mason, *J. Chem. Soc.*, 296 (1965).

(18) G. Natta, P. Corradini, and I. W. Bassi, *J. Am. Chem. Soc.*, **80**, 755 (1958).

(19) S. Watkins, Ph.D. Thesis, University of Wisconsin, 1967.

(20) The referees suggest that these compounds might be considered as complexes of the ligand S₂²⁻. We see no benefit of this formulation over that used here. The compounds are clearly not ionic, *i.e.*, M²⁺S₂²⁻, from their physical properties; a polar covalent bond presumably links the ligand and metal. In the same way, no benefit is derived from considering oxygen complexes^{15,16} as complexes of the peroxide ion O₂²⁻ rather than of O₂. The structural data,¹³ when published, will make the proposed formulation more logical. In the system ($\pi\text{-C}_5\text{H}_5$)₂NbS₂Cl the S-S distance is remarkably short (~1.7 Å) and suggestive of a S≡S bond; it certainly does not resemble the S-S bond distance predicted for an S₂²⁻ complex. On the other hand the lengthening of the O-O bond on complexing oxygen over the distance in molecular oxygen suggests that the ligand is approaching the state O₂²⁻.

analysis of this yellow compound indicated the formula $(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{CN}$. Although the complex is diamagnetic as seen by its sharp C_5H_5 proton nmr resonance signals, two structures might nevertheless be considered possible. The thiocyanate ion may have been degraded to yield a cyano complex $[(\pi\text{-C}_5\text{H}_5)_2\text{-NbS}_2\text{CN}]_n$ with niobium in the 5+ formal oxidation state. This formulation would be analogous to the other $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{X}]_n$ complexes. The possibility of a dimeric compound $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}(\text{SCN})]_2$ with niobium atoms in the 4+ formal oxidation state, and bridged by a disulfide linkage, cannot be ruled out entirely on the basis of magnetic behavior alone, however, since other niobium(IV) compounds are also known to be diamagnetic.^{21,22} A possible monomeric compound with a $\text{Nb}=\text{S}$ bond is unlikely because of the band at 520 cm^{-1} which we believed to be a S—S stretching frequency.

(21) See B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 109 (1964).

(22) L. F. Dahl and D. F. Wampler, *Acta Cryst.*, **15**, 903 (1962).

It is interesting that the infrared spectra of the polymeric substances $[(\pi\text{-C}_5\text{H}_5)_2\text{NbS}_2\text{Cl}]_n$ are more in accord with a geometry involving parallel rather than canted C_5H_5 rings.^{8,23} Thus in the 1000- and 820-cm^{-1} regions only single broad bands are observed. Of course the whole question of the geometry of $(\pi\text{-C}_5\text{H}_5)_2\text{-MX}_3$ systems is very much unsettled as yet.⁸ The main evidence for a canted ring structure rests on the proton nmr evidence for $(\pi\text{-C}_5\text{H}_5)_2\text{MH}_3^{n+}$ complexes ($\text{M} = \text{W}$, $n = 1+$; $\text{M} = \text{Ta}$, $n = 0$),²⁴ whereas the infrared evidence opposes this view. The question can best be settled by a crystallographic study.

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(23) H. P. Fritz, Y. Hristidu, H. Hummel, and R. Schneider, *Z. Naturforsch.*, **15b**, 419 (1960).

(24) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).