

Photochemistry of Cobalt(III) Tris-Chelate Complexes Containing a Co-S or Co-Se Bond

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Received April 13, 1981

The wavelength-dependent photochemistry of a series of sulfur- and selenium-containing Co(III) complexes is reported. The complexes are of the type $\text{Co}(\text{en})_2\text{L}^{n+}$, en denoting ethylenediamine and L being $\text{SCH}_2\text{CH}_2\text{NH}_2$ (CoSN), cysteine-*N,S*, $\text{S}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$ (CoMeSN), $\text{S}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{NH}_2$ (CoBzSN), $\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{S}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2$, cysteinesulfinate-*N,S*, $\text{SeCH}_2\text{CH}_2\text{NH}_2$ (CoSeN), and SeCH_2COO . Abbreviated designations for some of the complexes are given in parentheses. The photochemical behavior defines three groups: (a) thio and seleno complexes, which show only photoredox decomposition at all irradiation wavelengths; (b) thioether complexes, for which irradiation in the ligand field region leads to photoaquation while irradiation in the charge-transfer region gives both redox decomposition and aquation; and (c) the sulfinato complex, which shows linkage photoisomerization. Circular dichroism and magnetic circular dichroism, MCD, spectra are reported for CoSN, and the MCD spectra, for CoMeSN and CoSeN. The rates of the thermal back-reaction of the photoproducts are reported for CoMeSN and CoBzSN. Also, thermal reaction rates of CoMeSN and CoSN are given. The differences in photochemistry can be rationalized in terms of the presence or absence of an anisotropic π -donor interaction between Co(III) and the sulfur- or selenium-containing ligand.

Introduction

There have been a number of fairly recent reports on the syntheses, structure, and thermal reactivity of Co(III) chelate complexes of the type $\text{Co}(\text{en})_2\text{L}^{n+}$, where en is ethylenediamine and L denotes a chelating ligand containing a coordinating sulfur or selenium atom.¹⁻¹⁰ Many different sulfur- and selenium-containing ligands have been used, among them thio,^{1,2} thioether,^{1,3} seleno,⁴ sulfenato,⁶⁻⁸ and sulfinato^{6,9,10} in type.

We became interested in the photochemistry of such complexes because very little had been reported about the photoreactions of sulfur and selenium complexes in general and because this large family of $\text{Co}(\text{en})_2\text{L}^{n+}$ species provided a somewhat homologous series allowing the subtleties of ligand effects upon photochemistry to be studied. The structural and chemical characteristics of the ground state of these molecules are known, as is the photochemistry of a number of potentially related Co(III) acidoammine complexes,¹² so comparisons are possible. As an illustration, the isomerization and redox chemistry observed in the photolysis of $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$ ¹¹ is somewhat atypical of other Co(III) acidopentaammine complexes.

Recently, we reported preliminary results of our investigations of the photochemistry of thio, seleno, and thioether complexes¹³ and sulfinato complexes.¹⁴ The present paper adds detail as well as further results.

Experimental Section

Materials. All chemicals used in syntheses and analytical procedures were of a reagent grade unless otherwise stated.

Thiol Complexes. The complexes $\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$, "CoSN", and $\text{Co}(\text{en})_2(\text{cysteine-}N,S)^{2+}$, "CoCYS", were prepared according to literature procedures¹ and recrystallized as the perchlorate salts. The visible-UV absorption spectra agreed well with those published, although the molar extinction coefficients were about 10% higher than the reported values (see Table I).

Thioether Complexes. The complexes $\text{Co}(\text{en})_2[\text{S}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2]^{3+}$, "CoMeSN", and $\text{Co}(\text{en})_2[\text{S}(\text{CH}_2\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{NH}_2]^{3+}$, "CoBzSN", were prepared according to a published procedure.¹³ Careful purification by ion-exchange chromatography and recrystallization afforded perchlorate salts free of trace iodide. The absorption spectra agreed well with the published data (see Table I).¹³

Sulfenato Complex. The salt $[\text{Co}(\text{en})_2[\text{S}(\text{O})\text{CH}_2\text{CH}_2\text{NH}_2]](\text{NO}_3)_2$ was provided by E. Deutsch (University of Cincinnati); we designate the complex ion as "CoSON". Solutions of CoSON were always chromatographed on an ion-exchange column before use, although the absorption spectrum (Table I) agreed well with the published data.⁸

Sulfinato Complexes. The ions $\text{Co}(\text{en})_2[\text{S}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$, "CoSOON", and $\text{Co}(\text{en})_2(\text{cysteinesulfinate-}N,S)^{2+}$, "CoCYSOON", were prepared according to a published procedure.^{6,9} In the case of CoCYSOON, peroxide oxidation of CoCYS was carried out in 1 M perchloric acid instead of in neutral solution, and the reaction was essentially complete in 20 min. Recrystallization yielded perchlorate salts whose absorption spectra agreed well with previous data (see Table I).^{6,9}

Seleno Complexes. The compounds $[\text{Co}(\text{en})_2(\text{SeCH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$ and $[\text{Co}(\text{en})_2(\text{SeCH}_2\text{COO})](\text{ClO}_4)$ were kindly provided by E. Deutsch. The respective complexes are designated here as "CoSeN" and "CoSeO". Although the absorption spectra agreed excellently with those published,⁷ solutions were always chromatographed by ion exchange before use.

(-)₄₃₆-CoSN. Optically active CoSN was obtained by fractional precipitation with *d*-(+)-tartrate anion. A slight stoichiometric excess of potassium tartrate was added to a hot, nearly saturated aqueous solution of $(\text{CoSN})(\text{ClO}_4)_2$. Potassium perchlorate was filtered off, and the amount of tartrate increased to a 2-fold excess. The solution was then slowly cooled, and the brown solid was collected at a point when less than half of the CoSN had precipitated. The solid was washed extensively with methanol and recrystallized from minimal hot water. The resulting microcrystalline solid had an absorption spectrum identical with that of racemic CoSN and a value of $[\alpha]^{25}_{436}$ of 670°. The large molar rotation is characteristic of Co(III) chelate complexes that are chiral about the cobalt ion¹⁶ (the actual value may be higher as we do not claim optical purity for our preparation).

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Table I. Absorption Spectral Data (nm) for the Complexes Studied

complex	abbrev	S(σ) or Se(σ) \rightarrow Co($d\sigma^*$) charge-transfer band (ϵ) ^a	L ₂ (ϵ)	L ₁ (ϵ)	L' (ϵ)
(en) ₂ Co(SCH ₂ CH ₂ NH ₂) ₂ ²⁺	CoSN	282 (15 600)	370 sh (335)	482 (154)	590 sh (60)
(en) ₂ Co(cysteinato-N,S) ²⁺	CoCYS	282 (16 200)	360 sh (325)	484 (133)	590 sh (50)
(en) ₂ Co(SeCH ₂ CH ₂ NH ₂) ₂ ²⁺	CoSeN	297 (18 500)	masked	490 (170)	625 sh (45)
(en) ₂ Co(SeCH COO) ⁺	CoSeO	295 (17 000)	masked	520 (150)	625 sh (40)
(en) ₂ Co[S(CH ₃)CH ₂ CH ₂ NH ₂] ₃ ³⁺	CoMeSN	282 (8300)	360 sh (200)	487 (177)	
(en) ₂ Co[S(CH ₂ C ₆ H ₅)CH ₂ CH ₂ NH ₂] ₃ ³⁺	CoBzSN	291 (9920)	masked	487 (182)	
(en) ₂ Co[S(O)CH ₂ CH ₂ NH ₂] ₂ ²⁺	CoSON	284 (3700) ^b	masked	472 (467)	
(en) ₂ Co[S(O) ₂ CH ₂ CH ₂ NH ₂] ₂ ²⁺	CoSOON	288 (14 200)	masked	432 (220)	
(en) ₂ Co[S(O) ₂ CH ₂ CH(COOH)NH ₂] ₂ ²⁺	CoCYSOON	287 (11 900)	masked	430 (190)	

^a M⁻¹ cm⁻¹. ^b There is another charge-transfer band at 365 nm (6700).

Photolyses. Mercury line wavelengths were obtained by using a PEK 150-W mercury lamp with an Oriol ¹/₄-m monochromator or a 10-nm band-pass interference filter. Typical incident light intensities were 10⁻⁸–10⁻⁷ einstein s⁻¹. For some irradiations, the blue and green wavelengths of a Coherent Radiation Model 52B argon ion laser were used, with a power of 0.1–0.2 W. Reineckate¹⁷ and ferrioxalate¹⁸ actinometries were used, as appropriate.

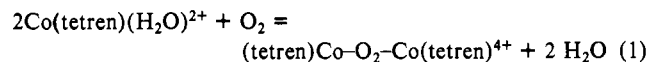
The photolyses were carried out in thermostated cells with temperature controlled to ± 0.5 °C. Typical complex concentrations were 10⁻⁴–10⁻³ M. All complexes except CoSON were photolyzed in 0.01 M perchloric acid to control ionic strength and to prevent secondary reactions of any Co(II) produced. CoSON was photolyzed at pH 3 with the ionic strength adjusted to 0.01 M with sodium perchlorate. Use of this pH minimized the acid-catalyzed thermal decomposition of this relatively less stable complex. Because of the low-disappearance quantum yields observed, photolysis times ranged from hours to days. Dark reactions were monitored concurrently and were found to be negligible under our experimental conditions. Quantum yields were based on about 10% overall photolysis to minimize possible secondary photolysis effects. Product analyses were performed at several degrees of photolysis, however, and were found to be consistent. Further, where present, isosbestic points were maintained well past 50% photolysis. Spectral changes were followed with a Beckman Acta MIV recording spectrophotometer. Loss of optical activity of the (-)-CoSN was monitored with a Perkin-Elmer 241 polarimeter.

Quantum Yield Calculations. Quantum yields for disappearance of starting material, ϕ , were calculated from the loss of charge-transfer, CT, absorption at ~ 290 nm. They were corrected for inner-filter effects and changing degree of light absorption when necessary. Reproducibility was better than $\pm 5\%$.

The yields for the production of Co(II), $\phi_{\text{Co(II)}}$, were obtained relative to ϕ by the quantitative determination of Co(II) (vide infra) in irradiated solutions at several degrees of photolysis, again with a reproducibility of $\pm 5\%$. In those cases where photoredox decomposition was the sole reaction, disappearance of all absorption features of the starting complex proceeded at the same rate, and plots of optical density, D , values for pairs of wavelengths, that is, of $D(\lambda_1)$ vs. $D(\lambda_2)$, were strictly linear as the photolysis proceeded, intercepting the point (0,0). This method was employed to infer the photoredox-only behavior of CoSON, which could not be subjected to Co(II) analysis because of the thermal instability of the complex at both low and high pHs.

Co(II) Analysis. We recommend the following method, which we believe to be new, as a very useful one for the detection of Co(II) at low concentrations and in complex mixtures. It is more sensitive than the Kitson method.¹⁹

The method makes use of the reactivity of Co(II) complexes of polydentate ligands such as tetraethylenepentamine, "tetren", with molecular oxygen:



Reaction 1, which is very fast, has an equilibrium constant of approximately 10¹⁵ M⁻¹ atm⁻¹ at room temperature.²⁰ The product

peroxy complex absorbs strongly with an extinction coefficient of 1.22 $\times 10^4$ M⁻¹ cm⁻¹ at $\lambda_{\text{max}} = 308$ nm, and the calibration curve with standard solutions was linear down to 4 $\times 10^{-6}$ M Co(II), with use of a 1-cm cell for the spectrophotometric analysis.

Our procedure was as follows. tetren (Strem Chemicals) was precipitated by the addition of concentrated hydrochloric acid and recrystallized repeatedly (four or more times) from ethanol/acetone until a pure white pentakis(hydrochloride) salt was obtained. The photolyzed solution (1–2 cm³) was diluted 1:1 with 0.1 M borate buffer (pH 8.5). To this solution was added 1 cm³ of aqueous tetren solution; the typical concentration was 10⁻³ M but was always sufficient to provide at least a 5-fold excess of tetren over total cobalt. In the cases of very low Co(II) concentration, a few crystals of solid tetren \cdot 5HCl were added directly, to avoid dilution. The solution was then oxygen saturated, with immediate formation of the brown μ -peroxy dimer occurring. The absorbance was measured at 308 nm. The reference solution was diluted equally with the borate buffer, but instead of tetren, a solution of sodium EDTA was added to prevent precipitation of Co(OH)₂, and the absorbance again was measured at 308 nm. Neither Co(EDTA)²⁻ nor borate buffer absorbs appreciably at this wavelength, and the difference in absorption between sample and reference is due only to the μ -peroxy species.

Two limitations to this method should be noted. First, it worked well in the presence of Co(III) complexes which are thermally stable at pH 8.5, but we found that solutions of CoSON were impossible to analyze because of the rapid decomposition of unphotolyzed complex under analysis conditions. Second, (tetren)Co–O₂–Co(tetren)⁴⁺ is not indefinitely stable but decays to mononuclear Co(III) products with a half-life of about 1 day at 30 °C.²¹ Solutions should therefore be analyzed soon after mixing. The decomposition is greatly slowed, however, if the solution is cooled, which, incidentally, further displaces the equilibrium of reaction 1 to the right. Cooling is advisable in the analysis of low Co(II) concentrations.

Analysis of Other Products. Photoaquation and isomerization products were isolated by ion-exchange chromatography over Sephadex SP-25 resin. The complex Co(en)₂(H₂O)(NH₂CH₂CH₂SR)³⁺, where R = CH₃ or benzyl, was identified by its absorption spectrum and chemical behavior, as described previously.¹³ The isomerization product Co(en)₂[OS(O)CH₂CH₂NH₂]₂²⁺, "CoOSON", was obtained as a red solid from an exhaustive photolysis and subsequent evaporation of solutions of CoSOON. Its purification and identification have been described.¹⁴ The analogous cysteinesulfinate complex, "CoOCYSON", obtained by photolysis of CoCYSOON, was identified by its spectral and chemical similarity to CoOSON. In all cases where photoaquation or isomerization was observed, only one Co(III) product was found. Quantum yields for the appearance of these products were therefore not determined directly but were assumed to be equal to $\phi - \phi_{\text{Co(II)}}$.

In the case of the CoSN, Folin's test for thiol²² showed no thiol photoproducts. The disulfide, cysteamine, was determined quantitatively in irradiated solutions (exhaustively photolyzed) by oxidative titration with bromate.²³ A calibration curve was made up, with use of 0.01 M perchloric acid solutions containing Co(ClO₄)₂, ethylenediamine, and cysteamine in the ratio 1:2:0.5. Neither Co(II) nor

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Table II. Quantum Yields for Photolysis of the Complexes^a

complex	λ , nm	ϕ	$\phi(\text{Co(II)})/\phi$
CoSN	254	1.6×10^{-2}	1.0
	313	1.77×10^{-3}	1.0
	366	1.68×10^{-3}	1.0
	405	1.79×10^{-3}	1.0
	436	1.48×10^{-3}	1.0
	457.9	2.48×10^{-4}	1.0
	488.0	1.24×10^{-4}	1.0
	514.5	2.83×10^{-5}	1.0
	577	2.83×10^{-5}	1.0
CoCYS	313	2.52×10^{-3}	1.0
	514.5	3.86×10^{-5}	1.0
CoSeO	313	7.40×10^{-2}	1.0
	514.5	5.01×10^{-3}	1.0
CoMeSN	313	1.01×10^{-2}	0.15
	514.5	7.55×10^{-5}	<0.02
CoBzSN	313	7.80×10^{-4}	0.48
	366	7.1×10^{-4}	0.45
	405	3.4×10^{-4}	0.27
	436	5.45×10^{-5}	<0.02
	514.5	2.32×10^{-5}	0.02
CoSON	313	9.1×10^{-3}	1.0
	366	8.9×10^{-3}	1.0
	514.5	5.38×10^{-4}	1.0
CoSOON	313	1.01×10^{-1}	trace (secondary photolysis)
	366	9.59×10^{-2}	0
	405	4.42×10^{-2}	0
	436	2.71×10^{-2}	0
	457.9	9.93×10^{-3}	0
CoCYSOON	313	8.3×10^{-2}	
	436	1.9×10^{-3}	

^a ϕ is the quantum yield for disappearance of starting complex, and $\phi(\text{Co(II)})$ is the quantum yield for production of Co(II). All photolyses were carried out at 26 °C and pH 2.0 except that for CoSON, which was at pH 3.0.

ethylenediamine appeared to affect the titration results.

Spectroscopic Data. Absorption spectra of CoSN as the BPh_4^- salt were obtained in spectroquality CH_2Cl_2 and absolute ethanol. Low-temperature spectra of poly(methyl methacrylate) films of $[\text{Co}(\text{SN})](\text{BPh}_4)_2$ were obtained on a Cary 17 recording spectrophotometer using a CTI Model 20 cryocooler at ca. 15 K. MCD spectra of CoSN, CoMeSN, and CoSeN were obtained in aqueous solution by using an instrument described elsewhere.²⁴ The CD spectra of resolved CoSN was obtained on the same instrument with the magnet removed.

Thermal Kinetics. The thermal decomposition of solutions of several of the complexes was studied. Since it was found that in every case both redox and aquation reactions involved loss of coordinated sulfur or selenium, disappearance of the ~290-nm charge-transfer band was monitored. Reactions were carried out in 10^{-2} M perchloric acid unless otherwise noted; temperatures ranging from 25 to 100 °C were obtained to better than ± 1 °C by immersion of the reaction cell in a large temperature bath. Although the typical reaction took days and in some cases weeks of data collection, all reactions were monitored over more than 2 half-lives and found to be strictly first order. Production of Co(II) was followed by using the μ -peroxo cobalt test described above.

Thermal return of photoproduct to starting material was studied in the cases where one-ended aquation or photoisomerization products were involved. After isolation or purification of the product by ion-exchange chromatography (the eluant was typically 10^{-2} M perchloric acid–0.3 M sodium perchlorate solution), re-formation of the starting material was followed through the increase in the ~290-nm CT absorption. Again, any production of Co(II) was determined by the μ -peroxo cobalt test.

Results

The quantum yield data are given in Table II. These were not affected by dissolved O_2 , by variation in light intensity over a 3–100-fold range, depending on the system, or by concen-

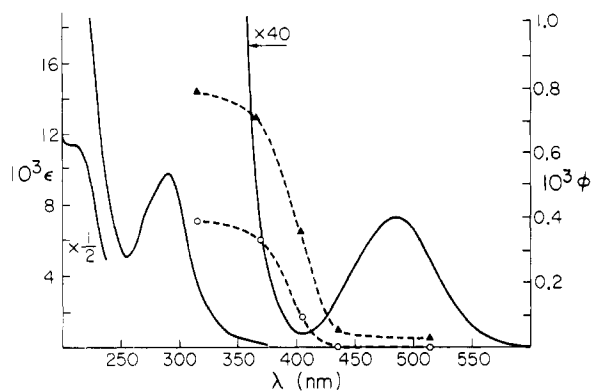


Figure 1. Absorption spectrum (—) of CoBzSN and wavelength dependence of ϕ (\blacktriangle) and $\phi(\text{Co(II)})$ (\circ).

tration of complex, in the range 1×10^{-5} to 2×10^{-3} M. As a general comment, irradiations around 515 nm led to ligand field excited states of octahedral T_{1g} parentage, while 313-nm region irradiations led to the $S(\sigma)$ or $Se(\sigma) \rightarrow \text{Co}(\sigma^*)$ CT transition, although some population of higher ligand field states may also have been involved. Also, disappearance quantum yields at this last wavelength are quite low by comparison to those reported by Orhavovic and Sutin¹¹ for $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$, very likely due to the chelate effect. The results group themselves into several classes.

CoMeSN and CoBzSN. The results are given in Table II, and the wavelength variation of the quantum yields for CoBzSN is shown in Figure 1. The sharp rise in both ϕ and $\phi_{\text{Co(II)}}$ with decreasing λ occurs at 400 nm and corresponds roughly to the onset of CT absorption. The general behavior of these thioether complexes is rather similar to that of the Co(III) acidopentaammine family.²⁵ Thus, irradiation of the CT band leads to both redox and aquation, whereas irradiation of ligand field absorption features leads to aquation only. The one-ended species $\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—SR})^{3+}$ was the only aquation product found.

It was found that this one-ended species reverted slowly back to the S-bonded starting material. For $R = \text{Me}$, the rate constant for the thermal return, k_r , was $2.3 \times 10^{-5} \text{ s}^{-1}$ at 55 °C and pH 2.0 and was negligible for pHs greater than 7. For $R = \text{Bz}$, $k_r = 1.02 \times 10^{-6} \text{ s}^{-1}$ at 65 °C, pH 2.0.

The thermal chemistry of the complexes is one of aquation to one-ended species; there is negligible Co(II) formation. For CoMeSN, k_a , the aquation rate constant, is ca. $1.7 \times 10^{-7} \text{ s}^{-1}$ at 92 °C, pH 2 (15% reaction after 270 h); the temperature dependence was not determined. The reaction is base catalyzed; k_a was found to be $2.2 \times 10^{-5} \text{ s}^{-1}$ at room temperature, pH 9. In the case of CoBzSN, the aquation rate was too slow (even at 100 °C) for quantitative data to be obtained.

CoSN, CoCYS, CoSeN, CoSeO, and CoSON. For this group of complexes the photochemistry consists of redox decomposition at all irradiation wavelengths (313–577 nm). CoSN was taken to be representative and was therefore studied in detail. As can be seen in Figure 2, ϕ increases sharply at about 450 nm, or at a significantly longer wavelength (about $6 \times 10^3 \text{ cm}^{-1}$ lower in energy) than that at the onset of the CT absorption. The yield is constant over the $S(\sigma) \rightarrow \text{Co}(\sigma^*)$ CT band but rises again in the wavelength region of the $N(\sigma) \rightarrow \text{Co}(\sigma^*)$ CT band.

The sulfur-containing product of the photoreaction was the disulfide cysteamine, and the ratio Co(II):cysteamine was found to be 1.88 ± 0.1 . Cysteamine could be produced either by dimerization of radicals or by attack of $\cdot\text{SCH}_2\text{CH}_2\text{NH}_2$ on

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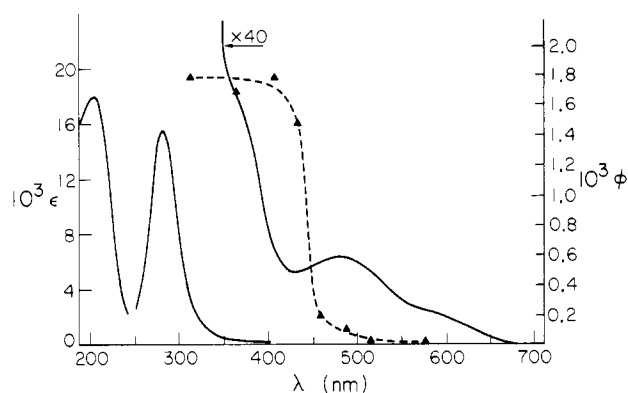


Figure 2. Absorption spectrum (—) of CoSN and wavelength dependence of ϕ (\blacktriangle) ($\phi = \phi(\text{Co(II)})$).

CoSN, and this latter possibility was investigated. Aqueous pH 2 solutions of 0.1 M (cysteamine) \cdot 2HCl and 10^{-4} M CoSN were either heated or photolyzed at 254 nm (where the disulfide absorbed >99% of the incident light), to effect homolytic S–S bond cleavage. The absorption features due to CoSN disappeared rapidly, with concomitant formation of Co(II), showing that attack by $\cdot\text{SCH}_2\text{CH}_2\text{NH}_2$ to form Co(II) (and probably cysteamine) is indeed a possible reaction. This sequence, if efficient, would lead to a 2:1 ratio of Co(II) to cysteamine, or essentially what was observed. We can, moreover, discount the alternative mechanism for cysteamine formation, that of radical combination, on the grounds that there was no detectable dependence of ϕ on the absorbed light intensity.

In an effort to probe the photoredox mechanism for CoSN, the optically active ($-$) $_{436}$ -CoSN complex was photolyzed. With either 313- or 515-nm irradiation, loss of optical activity proceeded at the same rate as did loss of starting material. There was evidently no geometrically labile intermediate in the photolysis sequence capable of regenerating CoSN. The thermal racemization, incidentally, is slow. None was detected after up to 10 days at room temperature.

The thermal chemistry of CoSN was found to be one of first-order redox decomposition (and *no* aquation). The rate constant is given by $k_r = 2.5 \times 10^{-16} \exp(16600/T)$.

The complex CoSON also exhibits only photoredox decomposition. The absorption spectrum shows two CT-type bands in addition to the $\text{N}(\sigma) \rightarrow \text{Co}(\sigma^*)$ one (see Table I). Irradiation into either band gave the same quantum yield, indicating that there is good communication between the two CT states. Presumably, then, both hands are $\text{S} \rightarrow \text{Co}$ charge transfer in type.

The thermal reaction of CoSON is also one of slow redox decomposition. In this case, however, the net behavior may be due to the fact that free sulfenate ion is extremely unstable in aqueous solution. If it were produced by a thermal aquation of the complex, it might well react either with original complex or with the aquo product to give redox products. A qualitative study indeed indicated that the thermal reaction did not follow simple first-order kinetics.

CoSOON and CoCYOON. For these complexes we find linkage isomerization as the sole photoreaction. Photolysis results in a nearly quantitative conversion to the thermodynamically less stable sulfinate-*O* complex. The details of the product characterization, in the case of CoSOON, have been reported.¹³ Although CoCYS and CoSON also have the potential for linkage isomerization, no evidence for such was found. In contrast, photolysis of $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$ is known to form significant amounts of the (in this case) thermodynamically more stable isothiocyanato isomer.¹¹

Returning to the case of CoSOON, irradiation at wavelengths greater than 350 nm led cleanly to the linkage isomer

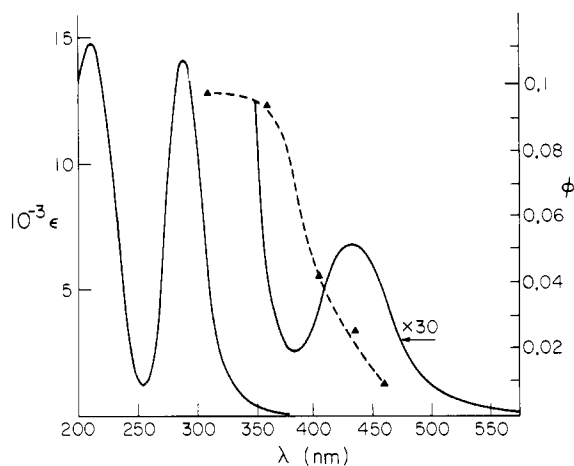


Figure 3. Absorption spectrum (—) of CoSOON and wavelength dependence of ϕ (\blacktriangle) ($\phi(\text{Co(II)}) \approx 0$).

with good maintenance of isosbestic points. No aquation products could be detected, nor was any Co(II) found. On 313-nm irradiation, however, isosbestic points were lost beginning at 70–80% photolysis, indicating that the sulfinate-*O* isomer has a low but nonzero quantum yield for photoreaction.

The variation of quantum yield with wavelength of irradiation is shown in Figure 3. There is a broader and less dramatic threshold than in the cases of CoSN and CoBzSN, and the threshold appears to be at a longer wavelength than that of the onset of CT absorption. However, the relatively high absorbance in the threshold region (400–500 nm) suggests that some type of weak CT absorption may be present. Also, because of the strong ligand field in this complex (*vide infra*), the position of the first ligand field band is not well separated from the CT bands, increasing the difficulty in determining the significance of the threshold behavior.

The thermal reaction of CoSOON was not studied in detail. The reaction is slow, and at 70 °C, pH 2.0, disappearance of complex (i.e., disappearance of the CT features) was accompanied by 44% Co(II) production. As described in ref 14 however, the *photoproduct* cleanly reverts to the CoSOON starting complex.

Spectroscopic Observations. The absorption spectra of the complexes are shown in part in Figures 1–3 and are summarized in Table I (see also ref 13). All have an intense $\text{N}(\sigma) \rightarrow \text{Co}(\sigma^*)$ band at ca. 210 nm and a $\text{S}(\sigma)$ or $\text{Se}(\sigma) \rightarrow \text{Co}(\sigma^*)$ band in the 280–300-nm region. In addition, the sulfenate complex, CoSON, has a third transition of intensity comparable to those above, in the 365-nm region, and characteristic of sulfenate complexes in general.^{6,8} Because of the wavelength profile of the CoSON photochemistry through the CT region, this third feature is most likely also due to some type of $\text{S} \rightarrow \text{Co}$ CT transition.

There are marked differences in the spectra in the ligand field region. Most obvious is the position of the first LF band, L_1 , of CoSOON as compared to those of the other complexes. Clearly, CoSOON has a much stronger ligand field strength than does the usual Co(III) acidoammine complex; this may be attributed to significant π back-bonding from the filled $\text{Co} d(\pi)$ orbitals to the $\text{S}=\text{O} \pi^*$ system. A similar but less efficient interaction in CoSON may account for the somewhat higher energy of the first LF band than those for the thio, seleno, and thioether complexes.

The second striking difference among the spectra is the presence of an extra shoulder, L' , on the low-energy side of the L_1 band in the cases of the thio and seleno complexes. The presence of the L' feature is characteristic of all analogous Co(III) thio and seleno complexes,^{1,2} is observed in the absorption spectrum of $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$,²⁶ and even appears

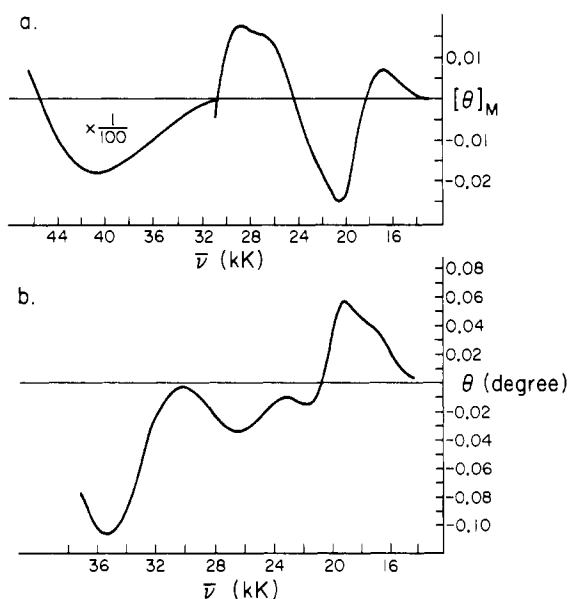


Figure 4. (a) MCD spectrum of CoSN aqueous solution. (b) CD spectrum of $(-)$ ₄₃₆-CoSN aqueous solution, d -(+)-tartrate salt ($1 \text{ kK} = 10^3 \text{ cm}^{-1}$).

in the absorption spectrum of the Cr(III) analogue of CoSN.²⁷ The feature is not present in the cases of the thioether and the sulfinato complexes. In the case of CoSON, however, the distinctly non-Gaussian shape of the low-energy side of the L_1 hints at the presence of the L' feature, and such a shoulder is clearly seen in the absorption spectrum of the cysteine-sulfinato analogue of CoSON.⁷

As a possible means of clarifying the nature of the L' band in CoSN, a poly(methyl methacrylate) film was made by evaporation of a methylene chloride solution of the tetraphenylborate salt of CoSN and poly(methyl methacrylate). The absorption spectrum of this film at 15 K showed a slight decrease in intensity throughout the region of wavelength above 400 nm, compared to the room-temperature spectrum. The L_1 maximum shifted from 482 to 478 nm on cooling. The decrease in intensity on cooling could be due to quenching of CT hot bands. The fact that the L' feature did not increase in peak intensity while narrowing in width is consistent with the transition being a vibronically allowed LF one, rather than an electric dipole allowed transition. Also consistent with this assignment as a LF band is the solvent effect on the spectrum of CoSN (as the tetraphenylborate salt). There is an increasing red shift in the $S(\sigma) \rightarrow \text{Co}(\sigma^*)$ CT band for the solvent sequence methanol, acetonitrile, and methylene chloride, this shift being 1000 cm^{-1} in the latter case. Yet neither the L_1 band nor the L' shoulder was affected either in position or in intensity.

The CD spectrum of $(-)$ ₄₃₆-CoSN and the MCD spectrum of racemic CoSN are shown in Figure 4. These spectra resolve the L' transition clearly and also show some unusual features compared to typical Co(III) acidoamine spectra. In particular, the positive MCD sign of L' and of the feature at higher energy is most unusual for Co(III) acidoamines.²⁸ More typical is the MCD spectrum of CoMeSN, shown in Figure 5, which displays only negative bands in the ligand field region. The MCD spectrum of CoSeN was found to be completely analogous to that of CoSN in both number and sign of the observed bands.

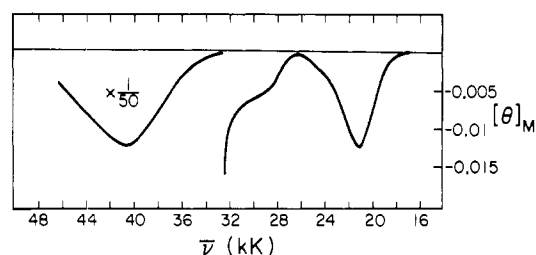


Figure 5. MCD spectrum of CoMeSN aqueous solution.

Discussion

The variety of both the thermal chemistry and the photochemistry reported here is remarkable for a group of complexes in which the coordinated atoms are nominally the same, and some attempted explanation is desirable. There are other similarities. The complexes are all thermally robust. The position of the $S(\sigma)$ or $\text{Se}(\sigma) \rightarrow \text{Co}(\sigma^*)$ transition does not vary much, which suggests that all have similar σ -bond strengths. Nor, with the expectation of CoSeO and CoSOON, is there great variation in the position of the L_1 band. One must look beyond these similarities to account for the differences in behavior.

One rationalization for the variety of photochemistry that we see can be made on the basis of the electronic structure of the Co-S or Co-Se moiety. The probability of similar σ -bond strength and the π -acceptor character of the sulfinato and sulfenato ligands has been noted above. A case will now be made for classifying thioether as a simple σ donor while attributing some degree of π -donor capacity to the thio, seleno, sulfenato, and sulfinato ligands.

In the case of the thio ligand, the 3s and 3p sulfur valence orbitals are filled, and it has been argued for some years that these orbitals are not appreciably hybridized in organic thiols. Recently, ab initio calculations of HS^- coordinated to Fe(II) have supported this conclusion.²⁹ Two p orbitals are used in Fe-S and S-H bonding, while the lone-pair electrons reside in an s-like orbital and a p-like orbital, which are spatially quite dissimilar. Even less hybridization would be expected in the case of seleno 4s and 4p orbitals.

When thio is converted to thioether by alkylation, it seems reasonable that the new S-R bond utilizes the remaining sulfur 3p orbital rather than the less accessible 3s orbital. The principal electronic structural difference between thio and thioether ligands is thus the presence or absence of a lone pair of electrons in a 3p orbital. Because of the negative charge on the thio ligand, this orbital has a radial extension large enough to overlap significantly with the filled $d(\pi)$ orbitals on the cobalt center (by analogy to the orbitals calculated in ref 29), but because of the geometry imposed by the chelating nature of the ligand, it must necessarily overlap unequally with d_{xz} and d_{yz} . This in turn must split the energetic degeneracy of these two d orbitals, resulting in a splitting of all ligand field transitions involving this orbital pair. Note that perturbation of Co $d(\pi)$ orbitals by a filled sulfur 3s orbital cannot cause a splitting, due to the spherical symmetry of the perturbing orbital.

In low-spin d^6 complexes of nominal C_{4v} symmetry where the unique axis contains the weaker field ligand(s), the lowest ligand field transition is ${}^1A_1 \rightarrow {}^1E$.³¹ The atomic orbital description of this transition is that an electron from the degenerate metal $d(\pi)$ orbital set is promoted to the $d_{z^2}(\sigma^*)$ orbital. A splitting of the $d(\pi)$ orbital set would split this transition into two nondegenerate ones, and such a splitting would account nicely for the observed L' shoulder in the thio and seleno complexes. In the thioether complexes where no

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sulfur 3p orbital is present to disrupt the degeneracy of the cobalt $d(\pi)$ orbitals, the ${}^1A_1 \rightarrow {}^1E$ transition would not be split, and no shoulder is observed. Thiocyanate would be classed with the thio and seleno complexes on the basis of its absorption spectrum,²⁶ which clearly shows the L' feature.

Some words must be said about the interpretation of the ligand field spectra of Co(III) thio and thiocyanate complexes by various authors. Kothari and Busch¹⁵ assigned the spectrum of the newly made CoCYS and, without comment, attributed L_1 and L' to the " ${}^1A_{1g} \rightarrow {}^1A_{2g}$ " and " ${}^1A_{1g} \rightarrow {}^1E_g$ " transitions derived from the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transitions in O_h symmetry, respectively. In their interpretation of the absorption spectrum of $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$, Buckingham et al.²⁶ made the same assignment of the analogous spectral features. Their rationalization was based upon the calculation by Piper and Wentworth³⁰ that ${}^1A_1 \rightarrow {}^1A_2$ should occur at the same energy as the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the octahedral parent complex, in this case, $\text{Co}(\text{NH}_3)_6^{3+}$. The ${}^1A_1 \rightarrow {}^1E$ transition should move to lower energy. Unfortunately, they used an incorrect value for the band maximum of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition for $\text{Co}(\text{NH}_3)_6^{3+}$, which is at 475 nm³⁰ and not at 490 nm. The former value is nearly 2000 cm^{-1} higher in energy than is the L_1 maximum at 518 nm observed for $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$, and the assignment of L_1 as due to the ${}^1A_1 \rightarrow {}^1A_2$ transition becomes questionable. We prefer our interpretation.

In the case of the Co-S and Co-Se chelate complexes discussed here, the parent complex $\text{Co}(\text{en})_3^{3+}$ has its L_1 band maximum at 466 nm.³⁰ The MCD and CD spectra of CoSN (Figure 4) and the MCD spectrum of CoSeN (Figure 5) clearly show a transition in this region, in addition to two transitions at lower energy. In the MCD spectra, this transition appears as a shoulder of negative sign, while in the CD spectrum of CoSN, the band is resolved because of its opposite sign with respect to the lower energy transition. The MCD spectrum of CoMeSN (Figure 5) also shows a shoulder on the high energy side of L_1 , at about 460 nm. We prefer to assign this band in all three complexes as the ${}^1A_1 \rightarrow {}^1A_2$ transition. In CoMeSN, the L_1 maximum is then assigned to the ${}^1A_1 \rightarrow {}^1E$ transition expected in C_{4v} symmetry. In CoSN, CoSeN, and $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$, the two lower energy bands, L_1 and L' , are the two nondegenerate components of the ${}^1A_1 \rightarrow {}^1E$ transition.

In the case of CoSON, the disposition of the sulfur electrons is clearly different from that of either the thio or thioether complexes. A lone pair of electrons is present, but it is probably in an s-like orbital, since acid/base data support protonation of oxygen rather than sulfur at very low pH.⁸ However, the $\text{S}=\text{O}$ π system is a source of electron density that could cause a perturbation of Co $d(\pi)$ orbitals, similar to that postulated for thio and seleno ligands. Although the L' band is not as clearly seen in CoSON as in CoSN, its presence is discernible in the spectrum of the analogous CoCYSON complex and can be attributed to the same splitting of the ${}^1A_1 \rightarrow {}^1E$ transition. The splitting is smaller, indicative of a smaller perturbation by the $\text{S}=\text{O}$ π system than by a lone pair of electrons. The $\text{S}=\text{O}$ π systems of the sulfinate represented by CoSOON should have a similar effect, but it should be even less strong since the wider spatial distribution of π -electron density in sulfinate makes it a less anisotropic π donor than sulfenate. Thus, any splitting of the lowest ligand field state would not be as pronounced in CoSOON and probably not be detectable by any ordinary inspection of the absorption spectrum.

The implications of π -donor interaction between the sulfur- or selenium-containing ligand and Co(III) are several. Of greatest importance is the expectation that $\text{S}(\pi)$ or $\text{Se}(\pi) \rightarrow$

$\text{Co}(\sigma^*)$ transitions should occur at lower energy than the $\sigma \rightarrow \sigma^*$ transitions. The former should be weak unless some unlikely intensity-stealing mechanism allows them to gain from the $\sigma \rightarrow \sigma^*$ CT band.³⁰ They are not excluded from photochemical reaction mechanisms, however, since they could be reached from other CT or even from ligand field states populated on irradiation. Nonspectroscopic CT states have been invoked to explain the anomalous threshold behavior of the photochemistry of $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$ ³² and $\text{Co}(\text{NH}_3)_5(\text{SCN})^{2+}$,¹¹ where redox photochemistry occurs at ligand field irradiation wavelengths; that is, the threshold for redox decomposition does not correspond to the onset of CT absorption. CoSN exhibits this anomalous behavior, but the thioether complex does not.

It is also possible that π -donor interaction introduces some amount of CT character into the LF excited states and even into the ground states of the complexes for which it is present. It does not seem coincidental that the thioether complexes, considered to be simple σ donors, have no thermal redox decomposition chemistry, no structural trans effect,³ and show no redox photochemistry at LF transition wavelengths. Nor does it seem coincidental that thio,² seleno,⁴ sulfenato,⁸ and sulfinato⁹ complexes all show a structural trans effect, thermally decompose either wholly or partially via intramolecular redox decomposition, and undergo no photoaquation upon irradiation of LF features. If substantial CT character is imparted to states not normally considered to be CT, it is possible that the thermal chemistry and photochemistry of these states will resemble those of CT states rather than the chemistry normally expected.

On the basis of π -donor arguments and the lack of photoaquation chemistry, we have grouped the sulfinate complexes with the other donors. It is important to note that the linkage photoisomerization of CoSOON and CoCYSOON is analogous to the nitro-to-nitrito linkage isomerization observed for $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$.³² In this case, isomerization via an aquo intermediate has been experimentally excluded (although not via a cage process), and the reaction is thought to take place from a low-lying CT state, presumably through cage recombination of primary redox products. Another resemblance with the photochemistry of CoSOON is that the ratio of photo-products is wavelength invariant and does not relate to the onset of CT absorption. In both complexes, the separation of CT and LF states (and ligand-localized states in the case of $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$) is not very good. For these reasons, the photochemical isomerization of CoSOON can be rationalized as taking place from a CT state that is not that of the $\text{S}(\sigma) \rightarrow \text{Co}(\sigma^*)$ transition, via cage recombination of redox products.

Summary

We have divided the sulfur- and selenium-containing Co(III) complexes investigated here into three groups: (a) thio and seleno complexes, (b) thioether complexes, and (c) sulfinate complexes, with group c possibly merely a subgroup of (a). The differences in photochemistry can be rationalized in terms of the presence or absence of an anisotropic π -donor interaction between Co(III) and the sulfur or selenium ligand. In the cases of the sulfenato and sulfinate complexes, where simultaneous π -donor and -acceptor interactions occur, the latter role appears to be less important in determining the photochemical behavior.

The variation in photochemistry among these complexes belies the apparent similarity of the Co-S or Co-Se bond. Clearly, the entire sulfur- or selenium-containing moiety is the photochemically important species and not just the coordi-

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nating atom, and the, in some cases, relatively small spectral differences reflect chemically important variations in excited-state properties.

Acknowledgment. We wish to thank Dr. E. Deutsch for the generous gift of several complexes and for many helpful suggestions. We also acknowledge the help of Dr. P. Stephens in obtaining the CD and MCD spectra and Dr. V. Miskowski

for the low-temperature spectral measurements. H.M. acknowledges a Swiss Federal Fellowship. This investigation was supported in part by a grant from the U.S. National Science Foundation.

Registry No. CoSN, 42901-32-6; CoCYS, 63058-94-6; CoSeN, 58866-01-6; CoSeO, 58866-04-9; CoMeSN, 35594-86-6; CoBzSN, 65622-67-5; CoSON, 68645-75-0; CoSOON, 75249-42-2; CoCYS-OON, 62698-05-9; (-)₄₃₆-CoSN, *d*-(+)-tartrate salt, 79171-30-5.

Contribution from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Parc Valrose, 06034 Nice, France

Molybdenum(0) and Tungsten(0) Adducts of Some Bicyclic Aminophosphanes Having a P-N Bond in a Constrained Structure

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Received April 7, 1981

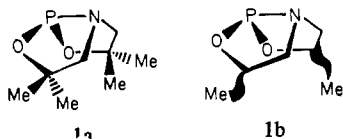
The coordination abilities of the bicyclic aminophosphanes **1a** and **1b**, which have P-N bonds in a strained structure that maintains both phosphorus and nitrogen atoms in a pyramidal configuration, have been evaluated with Mo(0) and W(0) carbonyls. A series of stable $M(\text{CO})_6L_n$ adducts has been synthesized with $M = \text{Mo}$ or W , $n = 1-3$, $L = \mathbf{1a}$ or $\mathbf{1b}$, from $M(\text{CO})_5(\text{pyridine})$, $M(\text{CO})_4(\text{norbornadiene})$, and $M(\text{CO})_3(\text{mesitylene})$. The ligands are coordinated through phosphorus only, as evidenced by the $\delta(^{31}\text{P})$ displacements, the $J_{31\text{P}-95\text{W}} = 210$ Hz or $J_{31\text{P}-183\text{W}} \approx 370$ Hz couplings, and the $\nu(\text{CO})$ vibration patterns. Low steric requirements (the *cis*- $M(\text{CO})_4(\text{bcap})_2$ and *fac*- $M(\text{CO})_3(\text{bcap})_3$ isomers are formed readily and exclusively) and good π -accepting capabilities (on the basis of the high $\nu(\text{CO})$ absorption frequencies) are the outstanding characteristics of these constrained ligands. No evidence for coordination through the nitrogen atom was found.

Introduction

The coordinating ability of aminophosphanes in which nitrogen is directly bound to phosphorus is generally characterized by an increased donor character of the phosphorus atom at the expense of that of nitrogen. This and the planar configuration of the nitrogen atom, as well as the relatively shorter P-N bond lengths generally found, are usually interpreted as resulting from a $\text{Np}_\pi\text{-Pd}_\pi$ contribution to this bonding.¹

Little work has been devoted to *constrained aminophosphanes*, i.e., aminophosphanes in which the nitrogen atom is prevented from being coplanar with its substituents. This being unfavorable to the overlap of the π orbitals, it should decrease the σ -donor ability of phosphorus, increase its π -accepting character, and make the nitrogen recover part of its own donor character. The very few, usually unstable, examples of N-bound BH_3 or BF_3 aminophosphane adducts known belong to this category.²

In the bicyclic aminophosphanes **1**,³ abbreviated bcap, whose



coordinating properties are evaluated here, the nitrogen atom is forced to a pyramidal configuration as a consequence of the

pyramidal configuration of the phosphorus atom transmitted by the constraining bicyclic system. This decrease the $\text{p}_\pi\text{-d}_\pi$ interaction and hinders the draining of electron density from nitrogen toward phosphorus. The nitrogen atom of ligands **1** have indeed been shown to display a definite donor character by forming unusually stable adducts with BH_3 and BF_3 .²

Where the ligand ability of phosphorus is concerned, this lowering of its σ -donor contribution due to the constrained structure could be partly compensated by the increased π character of the lone pair, by an increased π -acceptor character, and by a reduced cone angle at phosphorus, although the presence of one or two methyl groups on the carbon atoms α to the oxygen atoms may contribute to steric hindrance. The electron-withdrawing character of the oxygens is also expected to enhance the π -acceptor character of these ligands.

The aim of this study is to evaluate the coordinating properties of ligands **1** toward some low-valent transition-metal derivatives in order to situate their π -accepting character with respect to related ligands.⁴⁻⁷ The choice of the rather soft molybdenum(0) and tungsten(0) carbonyls was further dictated by the surprising fact that the sole known example of coordination of a metal by a tricoordinated nitrogen atom bound to phosphorus has been observed in a tungsten carbonyl derivative of a phosphonitrilic compound.⁸ In all the other cases reported so far, ligands having a P-N bond have been found to coordinate through phosphorus only.⁹

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