observed frequencies and their assignments are summarized in Table II. The spectra are in excellent agreement with those previously reported for the NF_4^+ cation[1] and the BiF_6^- [7,11,12] and SbF_6^- [7,12-15] anions, thus confirming the ionic nature of these adducts. By analogy with the previously studied[1] NF_4^+ salts, the degeneracy of some of the modes is lifted and crystal field splittings are observed. For example, the antisymmetric NF_4^+ stretching mode ν_3 (F_2) is split into three components, and the ν_3 (F_{1u}) and the ν_2 (E_g) modes of SbF_6^- show a splitting into three and two components, respectively. The presence of polyanions, such as $Bi_2F_{11}^-$,[7] in the $NF_4BiF_6 \cdot nBiF_5$ adducts is apparent from the appearance of a medium intense infrared band at 452 cm^{-1}, which is attributed to the stretching mode of the Bi–F–Bi bridge. Furthermore, additional bands were observed in the region of the BiF stretching and deformation modes. The maximum of the most intense BiF stretching infrared band was found to vary somewhat from sample to sample and varied from 575 to 605 cm^{-1}. In addition, some of the pyrolysis products showed weak infrared bands at 475 and 400 cm^{-1}. A comparison of the spectra of NF_4BiF_6 and $NF_4BiF_6 \cdot nBiF_5$ with those of NF_4SbF_6 and $NF_4Sb_2F_{11}$[1] shows a similar pattern for both when going from MF_6^- to $M_2F_{11}^-$.

Summary

The new NF_4^+ salt NF_4BiF_6 was prepared by the reaction between equimolar amounts of NF_4BF_4 and BiF_5 either at 180 °C without solvent or at 20 °C in HF solution. A salt of the composition $NF_4BiF_6 \cdot nBiF_5$ (n = 0.6–1.5) was prepared directly from NF_3, F_2, and BiF_5 at elevated temperature and pressure. It was converted to NF_4BiF_6 by vacuum pyrolysis at 280 °C. The salts were characterized by elemental analyses and vibrational spectroscopy, and their hydrolyses were studied. The pyrolysis of $NF_4SbF_6 \cdot nSbF_5$ to NF_4SbF_6 was briefly investigated, and the vibrational spectrum and x-ray powder pattern of NF_4SbF_6 are reported.

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Registry No. NF_4BiF_6, 61587-71-1; NF_4SbF_6, 16871-76-4; α-BiF_5, 7787-62-4; $NF_4Sb_2F_{11}$, 58702-89-9.

Supplementary Material Available: Tables III and IV, listing the observed x-ray powder diffraction patterns of NF_4BiF_6 and NF_4SbF_6 (2 pages). Ordering information is given on any current masthead page.

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Reactions of Cyanogen with Zerovalent Nickel Complexes

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Earlier[2a] we reported the reactions of HCN with NiL_4 complexes (L = phosphorus ligand) by eq 1. We now wish

$$HCN + NiL_4 \rightleftharpoons HNiL_3CN + L \qquad (1)$$

to report the results of an analogous study of cyanogen reactions (eq 2), where C–C rather than C–H bond cleavage

$$NCCN + NiL_4 \rightleftharpoons NiL_3(CN)_2 + L \qquad (2)$$

is the major reaction.

There appear to be only four reports[2b-5] in the literature on the reactions of cyanogen with transition metal complexes, with two brief reports involving Ni(0).[4,5] Nickel dicyanide complexes are of course well-known, though they have usually been prepared from $Ni(CN)_2$. They have been extensively studied[6-10] (usually by VIS–UV spectroscopy) mainly in order to define the factors which control equilibrium 3. No ^{31}P

$$NiL_3(CN)_2 \overset{K_3}{\rightleftharpoons} NiL_2(CN)_2 + L \qquad (3)$$

NMR studies and only scattered IR data on nickel dicyanide complexes can be found in the literature. We began this study in order to see how changing the electronic[11] and steric[12] properties of L would affect the rates and products of the cyanogen reactions, for comparison with the HCN results.[2a] By following IR and $^{31}P\{^1H\}$ NMR spectra with time we have also been able in some cases to observe unstable (NCCN)-NiL_3[13] complexes.

In a typical reaction, 0.2 mmol of $Ni[P(OEt)_3]_4$ in 1.8 mL of toluene was allowed to react with 0.4 mmol of cyanogen in a 10-mm NMR tube. The solution gradually became yellow and the IR spectrum showed a new band growing in at 2115 cm^{-1}, assigned to ν_{CN} in *trans*-$Ni[P(OEt)_3]_3(CN)_2$. $^{31}P\{^1H\}$ spectra showed a decline of the $Ni[P(OEt)_3]_4$ resonance at −159.1 ppm and the appearance of a new broader resonance at −121.5 ppm, assigned the exchange average of free $P(OEt)_3$ and $Ni[P(OEt)_3]_3(CN)_2$. Figure 1a shows that cooling to −59 °C causes the product resonance to split into two in the expected 1:3 intensity ratio. Addition of free $P(OEt)_3$ simply enhances the intensity of the −136.6-ppm resonance in the −59 °C spectrum. The fact that the width (~90 Hz) of the −120-ppm resonance in the −28 °C spectrum is unaffected by the addition shows that the exchange goes by dissociation of a ligand from $NiL_3(CN)_2$ (eq 3), rather than by association.[14]

Though $Ni[P(OEt)_3]_2(CN)_2$ provides a pathway for ligand exchange, it is not present in solution to a spectroscopically significant extent. Thus the position of the average resonance at 25 °C before L addition (Table I) is in good agreement with that calculated from eq 4, where δ_1 and δ_3 are the chemical

$$\bar{\delta}_{calcd} = {}^1/_4\,[\delta_1 + 3\delta_3] \qquad (4)$$

shifts (in the low-temperature limit spectrum) of free L and $NiL_3(CN)_2$. The IR spectrum shows only bands of unreacted cyanogen (2150 cm^{-1}) and $Ni[P(OEt)_3]_3(CN)_2$.

Rapid exchange of free L with ligand in $NiL_3(CN)_2$ is observed in nearly all cases; Table I gives ^{31}P chemical shifts

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Table I. ^{31}P NMR Chemical Shifts (ppm)^a

Ligand	NiL_4	$(NCCN)NiL_3$	$NiL_3(CN)_2$	L	Temp, °C	$\bar{\delta}_{calcd}$
PCy_3	-37.6^b	-36.3^c	-36.3^c	-9.2		
PEt_3	-2.2^d		$(-1.0)^e$			$+3.9$
			-2.7	$+23.8$	-80	
PMe_3	21.9		(31.4)			$+31.0$
			$+19.9$	$+62.7$	-46	
PPh_2Me	-3.6		(9.7)			$+8.7$
			$+1.8^f$	$+27.9$	-50	
PPh_2OMe	-126.6		(-115.6)			-114.9
			-115.5	-113.2	-76	
$PPh(OEt)_2$	-162.0		$(-136.6)^g$			
			-135.9	-153.0	-50	
$P(O\text{-}i\text{-}Pr)_3$	-154.3		(-125.3)			-126.4^h
			-116.3	-137.4	-53	
$P(OEt)_3$	-159.1		(-121.5)			-122.3
			-118.2	-136.6	-59	
$P(OCH_2CH_2Cl)_3$	-156.5		$(-121)^g$			
			-117.4	-137.3		
$P(O\text{-}p\text{-}tol)_3$	-131.1	-139.8		-128.2		
$P(O\text{-}o\text{-}tol)_3$	-129.4^d	-135.9		-130.0		
$P(OCH_2)_3CPr$	-127.6			-96.2		
$P(OCH_2)_3CCl$	-150.4					

[a] Shifts are in toluene, upfield of 85% H_3PO_4, at +25 °C unless noted otherwise. Values in parentheses are for the exchange average at 25 °C. δ_{calcd} was determined by eq 4.
[b] Chemical shift of $(C_2H_4)Ni(PCy_3)_2$.
[c] Chemical shift of $Ni(PCy_3)_2(CN)_2$.
[d] Chemical shift at −50 °C, where dissociation is suppressed.
[e] On cooling to −59 °C the average resonance shifted to +3.9 ppm.
[f] Red crystals which formed on standing gave a satisfactory elemental analysis for $Ni(PPh_2Me)_3(CN)_2$. They gave this resonance but not free PPh_2Me when redissolved and the solution cooled to −50 °C.
[g] Less than the theoretical amount of free L was present because of its slow reaction with cyanogen.
[h] Calculated for the L:Ni ratio of 6:1 in this solution.

Table II. IR Frequencies (cm^{-1}) of ν_{CN} in Toluene

Ligand	$(NCCN)NiL_3$	$NiL_3(CN)_2$	$NiL_2(CN)_2$
PCy_3			2104
PEt_3	2232, 2066	2098	2108
PMe_3	2232, 2064	2101^a	
$PPhEt_2$		2100^b	2112^b
PPh_2Me		2104	2112
PPh_2OMe		2108	2116
$PPh(OEt)_2$		2112	
$P(O\text{-}i\text{-}Pr)_3$		2114	
$P(OEt)_3$		2115	
$P(OCH_2CH_2Cl)_3$		2121	
$P(O\text{-}p\text{-}tol)_3$	2215, 2088		
$P(O\text{-}o\text{-}tol)_3$	2215, 2089		
$P(OCH_2)_3CPr$			
Free NCCN	$2322,^c$ 2150		

[a] Frequencies of 2097 and 2106 cm^{-1} were reported[10] for the isolated $NiL_3(CN)_2$ and $NiL_2(CN)_2$ complexes in Nujol.
[b] Frequencies for the isolated complexes in $C_2H_4Cl_2$: P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, 6, 1036 (1967).
[c] Raman-active symmetric stretch from G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Inc., Princeton, N.J., 1964, p 294.

at +25 °C and at temperatures low enough to freeze out intermolecular exchange. An exception is L = PCy_3. $Ni(PCy_3)_2(CN)_2$, prepared by the reaction of $(C_2H_4)Ni(PCy_3)_2$, does not exchange with added PCy_3 and shows no tendency to form a five-coordinate complex even at low temperature, indicating a very large value of K_3. Consistent with this, the IR band at 2104 cm^{-1} is unaffected by added PCy_3.

PEt_3 provides an intermediate case. The solution shows two IR bands at ambient temperature at 2098 and 2108 cm^{-1}. The weaker lower frequency band is assigned to $Ni(PEt_3)_3(CN)_2$ and the stronger higher one to $Ni(PEt_3)_2(CN)_2$. Addition of PEt_3 shifts equilibrium 3 to favor the five-coordinate complex. The presence of a large amount of $NiL_2(CN)_2$ complex at 25 °C is consistent with the large difference between the ^{31}P chemical shift of the exchange-averaged peak and that calculated from eq 4. Cooling to −59 °C shifts the peak to the calculated position, showing that K_3 has a very small value at that temperature.

IR evidence for other $NiL_2(CN)_2$ complexes, present to a lesser extent, is given in Table II. The assignment is strongly supported by (1) the very good correlation in Figure 2 between ν_{CN} in $NiL_2(CN)_2$ or $NiL_3(CN)_2$ complexes and ν_{CO} in $Ni(CO)_3L$ (an excellent measure of phosphorus ligand electron donor–acceptor properties),[11] (2) the frequencies reported (Table II) for the isolated $NiL_3(CN)_2$ and $NiL_2(CN)_2$ complexes with L = PMe_3 and PPh_2Et, and (3) nearly identical values of ν_{CN} for $NiL_n(CN)_2$ and for the corresponding $HNiL_nCN$ complex.[2a]

The value of K_3 is clearly dominated by steric effects. PMe_3, which is electronically similar to PEt_3 and PCy_3 but has a much smaller ligand cone angle,[12] gives no spectroscopically detectable concentration of $NiL_2(CN)_2$.

$Ni[P(O\text{-}p\text{-}tol)_3]_4$ reacts with cyanogen to give $Ni(CN)_2$ as the final product, rather than $NiL_3(CN)_2$ or $NiL_2(CN)_2$. IR spectra show the gradual formation and decay[15] of an unstable intermediate with strong broad IR bands at 2215 and 2088 cm^{-1}, assigned to $(NCCN)Ni[P(O\text{-}p\text{-}tol)_3]_3$,[16] analogous to the (nitrile)NiL_3 complexes reported earlier.[17] The stoichiometry is demonstrated by the $^{31}P\{^1H\}$ spectrum, which shows free and coordinated $P(O\text{-}p\text{-}tol)_3$ in a 1:3 ratio in the early stages of reaction at 25 °C. $Ni(CN)_2$ precipitates as the intermediate decays, and $P(O\text{-}p\text{-}tol)_3$ is liberated into solution. Entirely analogous reactions occur with $Ni[P(O\text{-}o\text{-}tol)_3]_3$, except that this coordinatively unsaturated complex reacts instantaneously with cyanogen on mixing. Rapid addition of CO destroyed the bands at 2215 and 2089 cm^{-1}, giving a mixture of $Ni[P(O\text{-}o\text{-}tol)_3]_3(CO)$ and $Ni[P(O\text{-}o\text{-}tol)_3]_2(CO)_2$[12] and regenerating NCCN. This experiment shows that the cyanogen in the intermediate had not yet undergone C–C bond cleavage.

$Ni(PEt_3)_4$ and $Ni(PMe_3)_4$ both react rapidly with cyanogen. Although $NiL_n(CN)_2$ complexes were the major products detected as soon as IR spectra could be run, weak bands at about 2232 and 2065 cm^{-1} were observed which are assigned to $(NCCN)NiL_3$ complexes.[18] These but not the Ni(II) complexes were converted to nickel(0) carbonyl complexes by adding CO.

Some NiL_4 complexes [those with L = $PPh(OEt)_2$, $P(OCH_2CH_2Cl)_3$, $P(OCH_2)_3CPr$, and $P(OCH_2CCl_3)_3$] react

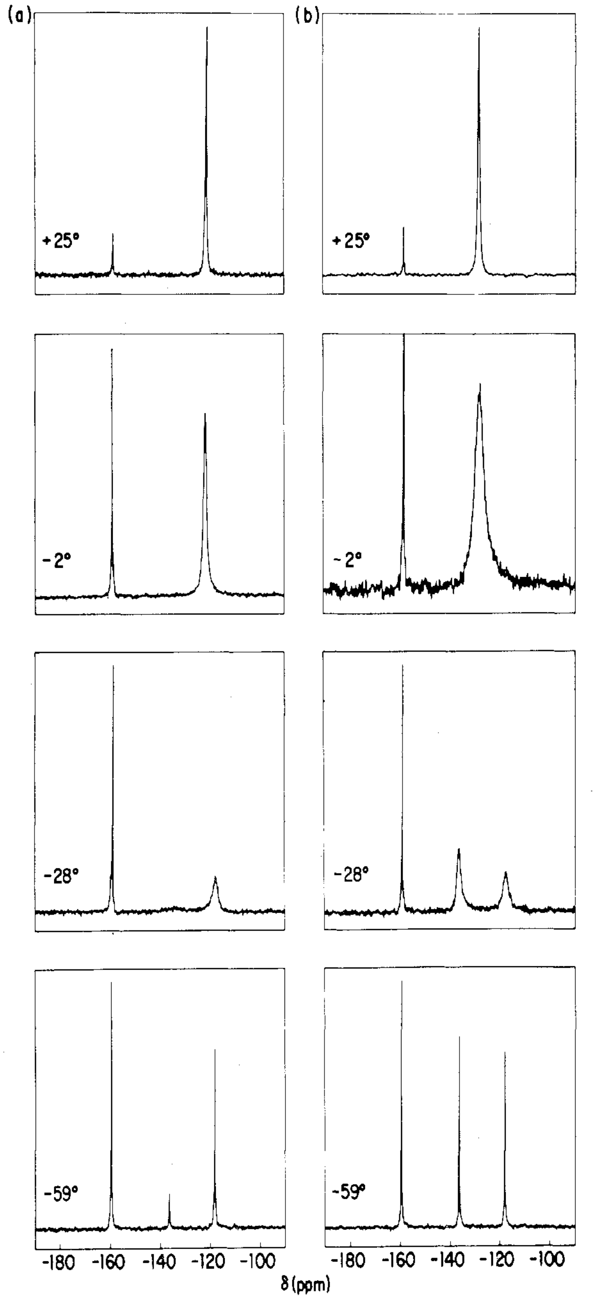

Figure 1. $^{31}P\{^1H\}$ spectra of a 1.8-mL toluene solution of 0.4 mmol of NCCN and 0.2 mmol of $Ni[P(OEt)_3]_4$ after 3 days at ambient temperature: (a) no additions; (b) with 0.3 mmol of added $P(OEt)_3$.

much more slowly with cyanogen than the others. ^{31}P and IR spectra showed so little reaction after 5 days, even with a 4:1 NCCN:NiL_4 ratio, that the solutions were allowed to stand a further 35 days in sealed tubes. While $Ni[PPh(OEt)_3]_4$ reacted nearly completely, $Ni[P(OCH_2CH_2Cl)_3]_4$ was largely unreacted. $Ni[P(OCH_2)_3CPr]_4$ reacted to an even smaller extent and gave $Ni(CN)_2$ and free $P(OCH_2)_3CPr$ as the only identifiable products. $Ni[P(OCH_2CCl_3)_3]_4$ did not react at all. These results suggest[19] that reaction 2 is an equilibrium which may lie well to the left for sufficiently small electronegative ligands. In support of this idea we found that heating $P(OEt)_3$ and $P(OCH_2)_3CPr$ with $Ni(CN)_2$ gave the NiL_4 complexes (identified by ^{31}P NMR). The solution of $P(OEt)_3$, but not that of $P(OCH_2)_3CPr$, also contained $NiL_3(CN)_2$.

Our experiments show the following: (1) cyanogen reacts most rapidly with those NiL_4 complexes which are extensively dissociated in solution or which are capable of rapid ligand dissociation;[20] i.e., coordinative unsaturation is a prerequisite for reaction; (2) the dissociation of $NiL_3(CN)_2$ to $NiL_2(CN)_2$ is favored by sterically bulky L; (3) initial reaction of cyanogen as a Lewis base rather than by oxidative addition is favored by a low electron density on the NiL_3; (4) sufficiently electronegative ligands dissociate after oxidative addition to precipitate $Ni(CN)_2$. This behavior is also observed for $Ni(CO)_4$.[2b] Reactions 1 and 2 are similarly favored by sterically bulky ligands which are good electron donors. The solution behavior in both cases is consistent with the 16- and 18-electron rule.[21]

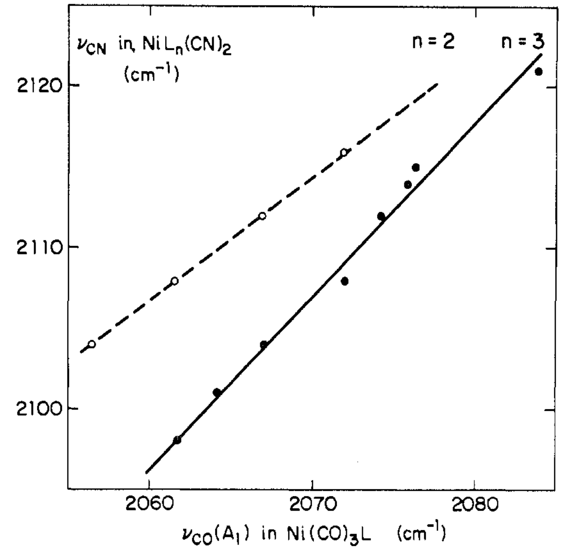

Figure 2. Infrared frequencies of ν_{CN} in $NiL_n(CN)_2$ in toluene plotted against $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ in CH_2Cl_2, from ref 11.

Experimental Section

$^{31}P\{^1H\}$ NMR spectra were recorded in FT mode using 10-mm tubes in a Brucker HFX 90 spectrometer with a Digilab FTS-3 data system. Chemical shifts are in ppm (positive upfield) from 85% H_3PO_4. Temperatures were determined by replacing the sample tube with another containing a concentric pentane thermometer in 2 mL of toluene. IR spectra were recorded using a 0.1-mm NaCl Barnes Engineering microcell (requiring ~25 μL of solution) in a Perkin-Elmer 221 spectrometer and were calibrated with CO gas (2143 cm^{-1}). VIS–UV spectra were recorded using a 0.1-mm serum-capped quartz cell in a Cary 14 spectrophotometer. The sample compartment was thermostated at 25 °C.

Literature procedures were used to prepare the NiL_4 complexes,[11,20] $Ni[P(O\text{-}o\text{-}tol)_3]_3$,[22] and $(C_2H_4)Ni(PCy_3)_2$.[23]

Cyanogen was added by syringe after freezing the toluene solutions of Ni(0) complexes in liquid N_2 and evacuating the syringe-capped tubes through a hypodermic needle. *Caution! Cyanogen is an extremely toxic gas and should always be handled in an adequate hood.* $Ni(PMe_3)_4$ and $Ni(PEt_3)_4$ spontaneously inflame in air. $P(OCH_2)_3CPr$ and its oxide are extremely toxic.

Reactions of anhydrous $Ni(CN)_2$ with phosphorus ligands were carried out with 0.5 mmol of $Ni(CN)_2$ and 2.0 mmol of L in 4 mL of toluene or *p*-dioxane. Glass tubes were frozen, evacuated, sealed, and left in a 100 °C oil bath for 11 weeks. They were then removed, cooled in dry ice, and opened in the hood. Small portions of chilled solution were taken by syringe and IR spectra run against a solvent reference. The samples were then filtered to remove unreacted solids and ^{31}P spectra run at +25 and −50 °C.

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Registry No. $(C_2H_4)Ni(PCy_3)_2$, 41685-59-0; $Ni(PEt_3)_4$, 51320-65-1; $Ni(PMe_3)_4$, 28069-69-4; $Ni(PPh_2Me)_4$, 25037-29-0; $Ni(PPh_2OMe)_4$, 41685-57-8; $Ni(PPh(OEt)_2)_4$, 22655-01-2; $Ni(P(O\text{-}i\text{-}Pr)_3)_4$, 14040-52-9; $Ni(P(OEt)_3)_4$, 14839-39-5; $Ni(P(OCH_2CH_2Cl)_3)_4$, 14512-93-7; $Ni(P(O\text{-}p\text{-}tol)_3)_4$, 14220-84-9; $Ni(P(O\text{-}o\text{-}tol)_3)_4$, 28800-00-2; $Ni(P(OCH_2)_3CPr)_4$, 61633-86-1; $Ni(P(OCH_2)_3CCl)_4$, 61633-87-2; $Ni(PCy_3)_2(CN)_2$, 61633-88-3; $Ni(PEt_3)_3(CN)_2$, 22806-37-7; $Ni(PMe_3)_3(CN)_2$, 21807-04-5; $Ni(PPh_2Me)_3(CN)_2$, 25464-08-8; $Ni(PPh_2OMe)_3(CN)_2$, 61633-89-4; $Ni(PPh(OEt)_2)_3(CN)_2$, 15282-55-0; $Ni(P(O\text{-}i\text{-}Pr)_3)_3(CN)_2$, 61633-90-7; $Ni(P(OEt)_3)_3(CN)_2$, 49756-79-8; $Ni(P(OCH_2CH_2Cl)_3)_3(CN)_2$, 61633-91-8; $(NCCN)Ni(P(O\text{-}p\text{-}tol)_3)_3$, 61634-12-6; $(NCCN)Ni(P(O\text{-}o\text{-}tol)_3)_3$, 61634-13-7; $(NCCN)Ni(PEt_3)_3$, 61665-40-5; $(NCCN)Ni(PMe_3)_3$, 61633-92-9; $Ni(PEt_3)_2(CN)_2$, 22806-42-4; $Ni(PPh_2Me)_2(CN)_2$, 61633-93-0; $Ni(PPh_2OMe)_2(CN)_2$, 61633-94-1; NCCN, 460-19-5.

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(13) We write the cyanogen–nickel(0) complex in this way to distinguish it from the Ni(II) complexes $NiL_n(CN)_2$ which contain two Ni–C bonds.
(14) Dissociative exchange of $NiL_3(CN)_2$ complexes has also been established by ^1H NMR studies by C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, **13**, 970 (1974).
(15) The intermediate reaches a maximum concentration in about 1 h at 25 °C. The UV spectrum of the intermediate shows an absorbance maximum at 390 μm ($\epsilon \sim 2 \times 10^3$).
(16) An unstable cyanogen complex of Rh(I) with IR bands at 2240 and 2090 cm^{-1} was reported in ref 5.
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(18) These complexes are so unstable and present in such low concentrations that they were not detected by ^{31}P NMR.
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A Light-Induced Redox Reaction of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I)

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Many complexes of Cu(I) have rather low-lying metal-to-ligand charge-transfer excited states and might be expected to participate in some interesting photoredox chemistry. We wish to report the light-induced redox reaction we have observed when a solution containing bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu(dmp)_2^+$, and *cis*-bis(iminodiacetato)cobaltate(III), *cis*-$Co(IDA)_2^-$, is irradiated at 454 nm, which corresponds to the absorption maximum of a metal-to-ligand charge-transfer band of $Cu(dmp)_2^+$.

Experimental Section

Preparation of Complexes. $Cu(dmp)_2BF_4$ was prepared from the 2,9-dimethyl-1,10-phenanthroline ligand (Aldrich, 99% grade) and reagent grade $CuSO_4{\cdot}5H_2O$ (Mallinckrodt) in an acetate-buffered 50:50 water–methanol mixture containing dissolved $NaBF_4$. After addition of ascorbic acid to effect reduction, evaporation of methanol yielded orange crystals of the complex. Analogous procedures afforded the nitrate and chloride salts of $Cu(dmp)_2^+$ as well. The purple complex K[*cis*-$Co(IDA)_2]{\cdot}1.5H_2O$ was prepared by a published method.[1] The purity of each complex was established by microanalysis. The cobalt complex was somewhat hygroscopic so that the concentration of *cis*-$Co(IDA)_2^-$ was determined from the absorbance at 562 nm. In agreement with ref 1, we found ϵ_{562} 152 $M^{-1}\ cm^{-1}$ for the cobalt complex.

Table I. Quantum Yields

[*cis*-Co-(IDA)$_2^-$], mM	10^3-$\Phi_{-Cu(I)}$[a]	[*cis*-Co-(IDA)$_2^-$], mM	10^3-$\Phi_{-Cu(I)}$[a]
1.42	1.53	4.71	5.24
1.49	1.86	4.95	5.55
1.50	1.71	5.00	3.78[b]
4.71	5.86	5.00	3.99[b]
4.71	5.70	9.39	11.30
4.71	5.43	9.39	11.61

[a] Except where indicated the solvent is 30% ethanol. [b] Solvent was 80% ethylene glycol.

Preparation of Solutions. In most experiments the solvent for the photolysis experiments was a 30:70 vol/vol mixture of ethanol–water which was 0.01 M in lithium acetate and 0.01 M in acetic acid. Some experiments involved a solvent which was 80% ethylene glycol and 20% water and which was 0.01 M in acetic acid and in lithium acetate. After the cobalt and copper complexes were added, the ionic strength was adjusted to $\mu = 0.1$ by addition of $LiNO_3$ or NaCl. Two different methods for degassing the photolysis solutions were employed. In some cases the solutions were repeatedly evacuated and refilled with scrubbed N_2 gas, while in others the solutions were continuously purged with argon during the photolysis.

Apparatus. Narrow-band irradiation (13 nm) centered at 454 nm ($\sim 1.8 \times 10^{16}$ photons/s) was achieved with a 1000-W xenon lamp, suitable filter, and a grating monochromator. The irradiated solutions were thermostated at 20 °C and for each cobalt concentration at least two photolyses were carried out. Absorption measurements were made on a Cary 15 spectrophotometer.

Analysis of Data. Ferrioxalate actinometry was used to measure incident light intensities.[2] The loss of Cu(I) was followed at 454 nm[3] and the appearance of Co(II) was monitored by the method of Kitson.[4] To calculate $\Phi_{-Cu(I)}$, the quantum efficiency for loss of $Cu(dmp)_2^+$, it was necessary to account for the change in the sample absorbance with time. In our experiments the reaction was pseudo first order in Co(III) so that the following differential equation described the rate of change of the absorbance due to loss of $Cu(dmp)_2^+$

$$\frac{-dA_{Cu}}{dt} = \frac{\epsilon l I_0 \Phi_{-Cu(I)}}{V}\left(\frac{A_{Cu}}{A_{Cu} + A_X}\right)(1 - 10^{-A_{Cu}}10^{-A_X})$$

In this expression A_X denotes the absorbance of other reactant and product species. The change in A_X was very small compared to the change in A_{Cu} and could be ignored. The other parameters include molar absorptivity ϵ of $Cu(dmp)_2^+$ at 454 nm, the path length l, the incident light intensity I_0, and the volume V of the photolyte solution. This equation may be integrated after separating the variables. Integrating the absorbance function over ΔA_{Cu}, the absorbance change observed in time Δt, and dividing by Δt yield $\Phi_{-Cu(I)}\epsilon l I_0/V$ from which we could extract $\Phi_{-Cu(I)}$. We used a numerical technique to integrate over A_{Cu}.

Results and Discussion

In a typical experiment, the initial absorbance of the $Cu(dmp)_2^+$ at 454 nm was about 1.7 and decreased smoothly upon irradiation as seen in Figure 1. In the dark the solutions showed no appreciable reaction over a time of at least several hours. Moreover, direct irradiation of solutions containing either *cis*-$Co(IDA)_2^-$ [5] or $Cu(dmp)_2^+$ [6] showed negligible photochemistry at 454 nm.

The quantum efficiency for loss of $Cu(dmp)_2^+$ increases with increasing cobalt concentration as seen in Table I. Owing to the smaller absorptivity of $Co(SCN)_4^{2-}$ and to overlap with the *cis*-$Co(IDA)_2^-$ spectrum the determination of the amount of Co(II) formed is less precise than the data for loss of Cu(I). Within the experimental error, ca. 8%, however, the formation