electron–magnon coupling.[14] Our experiments are consistent with this conclusion.

Turning our attention now to the maximum at 30,200 cm^{-1} in the spectrum of $NiCl_2$ we note that it is completely absent in $CdCl_2$–Ni^{2+}. On the surface this would tend to indicate an absorption process which is similar to that observed for the $^3A_{2g} \rightarrow {}^1A_{1g}$ absorption band. Indeed Kozielski, *et al.*,[4] have concluded that such is the case. Two phenomena dictate against this being either a short- or a long-range magnetic exchange process, however. The first is the total absence (in $CdCl_2$–Ni^{2+}) of the transition even though the weaker (in $NiCl_2$) $^1T_{1g}$ and $^1A_{1g}$ bands are present. Since the concentration of Ni^{2+} is 10% in the $CdBr_2$–Ni^{2+} spectrum shown and 7% in the $CdCl_2$–Ni^{2+} spectrum, considerable numbers of pairs should be present. It follows then that a pairwise interaction would produce a band at 30,200 cm^{-1}. Second, the band is observed even at 113°K. This is some 63°K above the Neel temperature of $NiCl_2$ and would seem to be much too high a temperature for even moderate-range order to exist. This suggests that this maximum arises from the presence of a cooperative interaction of a type other than a magnetic one. Because of a lack of polarization it is not possible to determine the exact nature of the interaction.

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Structure of Tungsten Oxytetrafluoride[1]

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Single-crystal X-ray intensity measurements on WOF_4 have been interpreted in terms of ordered tetrameric units with oxygen atoms assigned to the bridging positions.[2] The infrared spectrum of the solid showed a strong band at approximately 1050 cm^{-1} which the authors interpreted in terms of a W–F stretching frequency due to an abnormally short W–F bond. It has been pointed out that this assignment is inconsistent with vibrational assignments in similar transition metal oxyfluoride compounds[3] and alternate disordered structures containing fluorine bridges have been suggested for this material.[4] Unfortunately the X-ray measurements are not sufficiently accurate to distinguish between the various proposed models.

We have made infrared and nmr measurements on the solid phase which lend convincing support to a model containing fluorine at the bridging positions in the tetramer.

Infrared Data.—Oxygen-18-substituted WOF_4 was prepared by the reaction of WF_6 with $H_2{}^{18}O$ in the presence of HF and purified by sublimation. The composition of the material was established by single-crystal precession techniques. The infrared measurements were taken on a Perkin-Elmer 521 spectrometer from samples sublimed onto a CsCl window at liquid nitrogen temperature. The resulting spectrum shows the same structure in the region 500–750 cm^{-1} as do the previously published spectra.[2] In addition a strong peak appears at 997 cm^{-1} with a smaller peak at 1054 cm^{-1}. These peaks are, therefore, obviously due to W–^{18}O and W–^{16}O stretching frequencies, respectively.

Nuclear Magnetic Resonance.—A polycrystalline nmr sample was prepared by the same reaction and sealed in a polypropylene tube. At room temperature the ^{19}F resonance is dominated by a motionally narrowed line with a width of 200 mG; this is an indication of molecular motion at a rate in excess of 10^4 Hz. A spectrum without the narrowing is obtained at lower temperatures (−58 and −114°). The line recorded in the *CW* mode is 8 G wide and symmetric. Another line could be recorded only in the fast-passage mode because of extremely long spin–lattice relaxation time T_1 of between 3 and 4 min. In contrast, the first line has an estimated T_1 of 0.1 sec, three orders of magnitude shorter. From these observations we conclude that there are fluorine nuclei located in vastly different sites insofar as librational motion of WOF_4 is concerned; this is not consistent with a tetramer with all fluorines in terminal positions, no matter how chemically dissimilar those sites may be.

(1) This work performed under the auspices of the U. S. Atomic Energy Commission.

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Emission Lifetimes of Tungsten Carbonyl Complexes

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The behavior of excited states of coordination compounds has been investigated by studying photophysical processes, such as energy transfer[2–5] and radiative decay[6] as well as photochemistry.[7] However, development of models for structure–reactivity relationships has been slow because of the lack of absolute rate data. For example, variations in quantum yields for a measurable process may be due either to an increase in the rate constant for that process or to a decrease in the rate constant for some competitive process. The

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desired data can be obtained by various means, such as combination of measurements of both the intensities and lifetimes for emission or by flash kinetic studies. We wish to report work in which we use relative emission lifetimes as a reference to establish relative time scales for decay processes in a series of compounds having the structure $W(CO)_5(X)$, where X is a Lewis base containing a nitrogen or oxygen donor atom.

Experimental Section

Compounds.—All $W(CO)_5(X)$ complexes were prepared by photolysis of $W(CO)_6$ in the presence of low concentrations of the entering group X. The complexes were not usually isolated but were characterized in solution by their characteristic ir and uv spectra.[8] The preparations were carried out in luminescence-free methylcyclohexane, and the short irradiation times precluded formation of secondary photoproducts.

Lifetime Measurements.—The emission lifetimes were measured at 77°K in methylcyclohexane glasses using a TRW Model 31A lifetime machine. The source was a N_2 pulsed lamp with a flash time of approximately 20 nsec and pulsed at 5 Kc. The appropriate filters were used to reduce interference from scattered light. The emission decay curve was displayed on a Tektronix Type 556 oscilloscope and photographed. Plots of log (emission intensity) against time were linear for all complexes studied.

Emission Spectra.—Emission spectra were obtained at 77°K using an Aminco-Bowman emission spectrometer. When relative emission quantum yields were determined, absorbances of the samples were matched at 400 nm in room temperature solutions and the same sample cell was used for the emission spectrum. The observed change in the extinction coefficient of $W(CO)_5(py)$ in going from room temperature to 77°K was small.

Results and Discussion

The lifetimes of a number of $W(CO)_5(X)$ complexes are given in Table I. The lifetimes are consistent with the $^3E(e^3b_2{}^2a_1) \rightarrow {}^1A_1(e^4b_2{}^2)$ assignment for the emission of $W(CO)_5(X)$ complexes.[8] The relatively short lifetimes for these spin-forbidden emissions are similar to those for other heavy metal systems[6] and demonstrate the importance of spin–orbital coupling effects in the tungsten carbonyl system.[8,9] We found in an earlier study[8] that the energy of the $^3E \rightarrow {}^1A_1$ transition is nearly independent of X for the complexes in Table I. The emission lifetimes, however, span almost 2 orders of magnitude (6.5×10^{-7} to 2.6×10^{-5} sec).

TABLE I

LIFETIMES OF $W(CO)_5(X)$ COMPLEXES[a]

X amines	$10^6\tau$, sec	X amines	$10^6\tau$, sec
$EtNH_2$	0.92	$(Me)_2NH$	2.6
tert-$BuNH_2$	1.2	Piperidine	3.1
i-$PrNH_2$	0.65	$(Et)_2MeN$	25.5
c-$HxNH_2$	1.1	$(Et)_3N$	9.7
$(Et)_2NH$	5.1	$(n\text{-}Bu)_3N$	6.9
		$(Me)_2NCH(CH_2)Ph$	15.5
Oxygen donors		Oxygen donors	
EtOH	11.7	EtOEt	7.1
i-PrOH	6.6	Acetone	5.3
tert-Bu–OH	6.3	Acetone-d_6	5.7
		Cyclohexanone	3.6
Pyridines		Pyridines	
Pyridine	2.5	2-Methylpyridine	1.7
		2,4,6-Trimethylpyridine	11.7

[a] Temperature = 77°K; solvent is methylcyclohexane.

Equations 1–4 show reasonable mechanisms for decay of the metal carbonyl excited state. We assume

$$[W(CO)_5(X)]^* \xrightarrow{k_1} W(CO)_5(X) + \text{heat} \tag{1}$$

$$[W(CO)_5(X)]^* \xrightarrow{k_r} W(CO)_5(X) + \text{light} \tag{2}$$

$$[W(CO)_5(X)]^* \xrightarrow{k_3} W(CO)_5 + X \tag{3}$$

$$[W(CO)_5(X)]^* \xrightarrow{k_4} W(CO)_4(X) + CO \tag{4}$$

that all excited species decay by way of the ^3E state irrespective of excitation wavelength.[10] If the sum of the nonradiative decay rate constants is $k_1 + k_3 + k_4 = k_{nr}$, and the radiative decay rate constant is k_r, the lifetime of the excited state, τ, is given by eq 5 and the emission quantum yield is given by eq 6.[7] The variation in lifetimes in Table I could be due to changes in either k_{nr} or k_r or both, but at least it is certain that the ligand X must affect these changes.

$$\tau = \frac{1}{k_r + k_{nr}} \tag{5}$$

$$\Phi = \frac{k_r}{k_r + k_{nr}} \tag{6}$$

The rate constant for radiative decay can be estimated from the integrated absorption intensity using the Einstein law. Although there are examples which indicate that the relationship does not work well with some coordination compounds,[7] the emission spectra for complexes reported in Table I appear to be reasonably good mirror images of absorption which appears as a shoulder on the long wavelength side of the first, broad absorption band. As the absorption spectra of all the $W(CO)_5(X)$ complexes show similar positions, shapes, and molar absorptivities for the $^1A \rightarrow {}^3E$ band, we have chosen the expedient of taking the extinction coefficient at 438 nm (22.8 kK) as a measure of the *relative* rate constant for radiative decay. Selected examples shown in Table II show that variation in the absorbance values is smaller than the variation in lifetimes. Probably the most important source of variation in τ is variation in k_{nr}. The conclusion is confirmed by estimates of the relative quantum yields of emission, shown for three cases in Table II. Relative values of Φ were obtained by excitation at 400 nm, using solutions prepared to have equal absorbance at the excitation wavelength. The integrated areas under the emission curves were taken as proportional to Φ, a

TABLE II

ABSORPTION AND EMISSION DATA FOR $W(CO)_5(X)$ COMPLEXES

Compound	$^1A_1 \rightarrow {}^3E_1$ (ϵ), kK[a]	Rel absorption	Rel Φ[b]	$10^6\tau$, sec
$W(CO)_5(H_2N\text{-}c\text{-}Hx)$	22.8 (520)	1	1	1.1
$W(CO)_5(HNEt_2)$	22.8 (727)	1.4	6	5.1
$W(CO)_5((CH_3)_2NCH(CH_2)Ph)$	22.8 (1080)	2.1	12	15.5
$W(CO)_5(py)$	22.8 (630)	1.2		2.5
$W(CO)_5(CH_3COCH_3)$	22.2 (910)	1.8		5.3

[a] In hydrocarbon solvent at room temperature. [b] ±50%; emission maximum ≈ 530 nm.[8]

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(10) This is apparently not true at room temperature; *cf.* ref 6, p 345. However, at 77°K we have found that the emission quantum yield of $W(CO)_5(py)$ is independent of excitation wavelength.

good approximation in view of the fact that the emissions lie in the same spectral region.

Nonradiative decay rates vary considerably as X is changed, and the series in which the sixth ligand is an aliphatic amine is especially interesting. Decay rates tend to decrease as the number of hydrogen atoms attached to the nitrogen atom is decreased, *i.e.*, 1° > 2° > 3°. This is consistent with the general theory of Robinson and Frosch,[11] if we assume that N–H vibrations play an important role in the internal conversion process. The result is also reminiscent of the effect of successive substitution of methyl groups for hydrogen atoms on the nonradiative decay rates of the excited singlets[12] and triplets[13] of acetone and its derivatives. However, comparison of the results obtained with oxygen bases shows that other factors must be of importance since the longest lifetime observed with any oxy base was obtained with ethanol and there is no significant separation between the compounds which bear a hydrogen atom attached to the basic oxygen and those which do not.

In solution at room temperature the compounds all undergo photodissociation of the X ligands with high quantum yields and emission is totally quenched. The relationship between decay by chemical reaction and the fast nonradiative decay rates at low temperature is uncertain, but the processes may involve similar, or even identical, micromechanisms for internal conversion of electronic to vibrational energy.

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A Novel Form of Cobalt(II) Dioctylphosphinate

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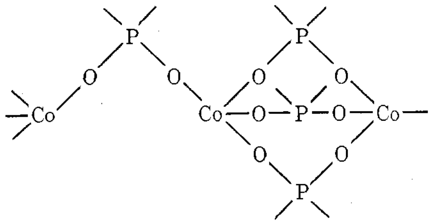
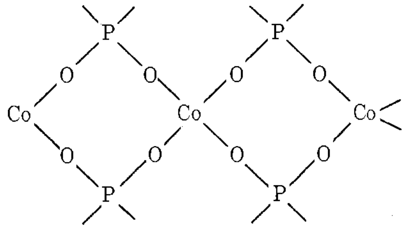
Different forms of cobalt(II) phosphinates have been studied in our laboratories[1] and elsewhere,[2] but all of the previously known compositions were reported to contain tetrahedral cobalt(II) and symmetrical bridging *O,O'*-phosphinate groups. Polymeric structures are formed, such as



or



The recent synthesis in our laboratories of a new form of cobalt(II) phosphinate which probably contains six-coordinate metal centers is therefore of considerable interest. This report presents the preparation and characterization of the new form of cobalt dioctylphosphinate and compares it to the tetrahedral form of this compound.

Experimental Section

Dioctylphosphinic acid, which was supplied by Hynes Chemical Research (Durham, N. C.), was purified by recrystallization from ethanol. Other chemicals and solvents were reagent grade and were used without further purification.

$Co[OP(C_8H_{17})_2O]_2$-I.—This material was prepared using the same general procedure as described for the previously reported tetrahedral phosphinates.[1] In one experiment 2.5 g of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.010 mol) in 100 ml of 95% ethanol was added with stirring to a solution containing 6.3 g of $(C_8H_{17})_2P(O)OH$ (0.022 mol) in 200 ml of 95% ethanol. A blue precipitate rapidly formed. The suspension was brought to boiling, an additional 100 ml of 95% ethanol was added, and the solvent was evaporated until the volume reached 100 ml. The suspension was then filtered, and the precipitate was dried under vacuum at 70° for 2 hr, yield 6.3 g. *Anal.* Calcd for $C_{32}H_{68}CoO_4P_2$: C, 60.27; H, 10.75; Co, 9.24; P, 9.72. Found: C, 59.71; H, 10.42; Co, 9.17; P, 10.23.

$Co[OP(C_8H_{17})_2O]_2$-II.—Anhydrous $CoCl_2$ (1.3 g, 0.010 mol) was combined with $(C_8H_{17})_2P(O)OH$ (6.09 g, 0.0217 mol) in 200 ml of absolute ethanol. The ethanol was distilled off, and the residue heated to 60° under vacuum for a short time. The residue was then washed with 95% ethanol and dried under vacuum for several hours. *Anal.* Calcd for $C_{32}H_{68}CoO_4P_2$: C, 60.27; H, 10.75; Co, 9.24; P, 9.72. Found: C, 60.36; H, 10.60; Co, 9.35; P, 9.82.

Visible spectra were recorded on a Perkin-Elmer Model 450 spectrophotometer. Solid samples were prepared as mulls with Nujol. Magnetic measurements were made on a standard Gouy balance. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. The samples were run as mulls with Nujol between KBr plates and as solutions in CCl_4. The X-ray powder patterns were obtained with a General Electric XRD-5 X-ray diffraction unit with vertical tube mount and standard General Electric 14.32 cm diameter cameras. The dsc curves were obtained on a Du Pont differential scanning calorimeter.

Results and Discussion

Previously $Co[OP(C_8H_{17})_2O]_2$ polymers (form I) were generally prepared from cobalt(II) acetate and dioctylphosphinic acid,[3] whereas the new form (form II) can be isolated from the reaction of cobalt(II) chloride and dioctylphosphinic acid. Since the substitution of potassium dioctylphosphinate for dioctylphosphinic acid has no effect on the outcome of either reaction, it appears that the cobalt salt starting material is the main factor in determining the form of the product.

The visible and near-infrared spectra of both forms are given in Figure 1. The fine structure and peak positions in the spectra of form I are quite consistent with the spectra of known tetrahedral cobalt(II) complexes

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