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Patterns of Photochemistry of a Cobalt(III) Complex Having a Co–S or Co–Se Bond

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We wish to report on the photochemistry of Co(III) chelate complexes containing two kinds of Co–S and Co–Se coordination. The complexes are of the type $Co(en)_2L^{n+}$, where en denotes ethylenediamine, and L = $H_2NCH_2CH_2S^-$ (CoSN), $H_2NCH_2CH_2SCH_3$ (CoMeSN), $H_2NCH_2CH_2SCH_2(C_6H_5)$ (CoBzSN), $H_2NCH_2CH_2Se^-$ (CoSeN), and $^-OOCCH_2CH_2Se^-$ (CoSeO).

CoSN, CoMeSN, and CoBzSN were prepared by published procedures [1, 2], CoSeN and CoSeO were kindly provided by E. Deutsch [3]. The absorption spectra shown in Figure 1 are similar. All show strong absorption in the 200 to 220 nm and 282–297 nm regions, presumably charge transfer in type (designated as CT_2 and CT_1, respectively), and which we assign as N(σ)LMCT and S(σ) or Se(σ)LMCT, respectively. It is noteworthy that the CT_1 band is observed in Co(III) complexes containing thiocyanato [4], thio [1], sulfenato [5], sulfinato [6], and sulfito [7] ligands, suggesting that the σ donating ability of all these ligands is about the same. The complexes all show a shoulder at ~370 nm and a maximum at ~490 nm, which we assign as the second and first ligand field bands, L_2 and L_1, respectively. In addition, however, the absorption spectra of CoSN, CoSeN, and CoSeO have a shoulder on the low energy side of the L_1 band.

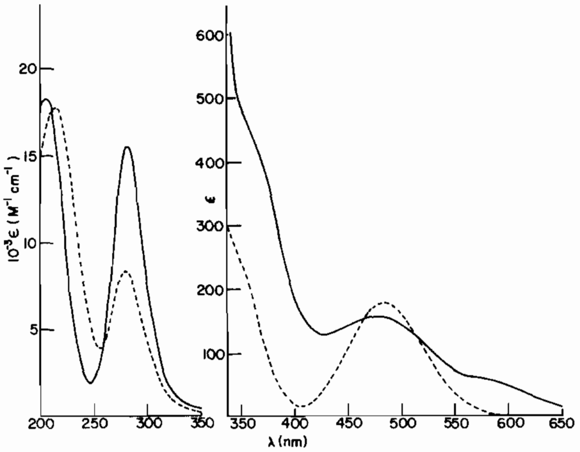

Fig. 1. Absorption spectrum for CoSN (full line) and CoMeSN (dashed line). Other CT_1 absorption maxima and extinction coefficients (λ, nm; ϵ, M^{-1} cm^{-1}): CoBzSN (291; 9,920), CoSeN (297; 18,500), CoSeO (295; 12,000). Other L_1 bands. CoBzSN (487; 182), CoSeN (490; 170), CoSeO (520; 150).

Quantum yields for disappearance of starting complex, ϕ_d, and for redox decomposition to give Co(II), ϕ_r, are given in Table I. The former were determined by the decay of the CT_1 band and the latter by analysis [8]. As can be seen, redox decomposition is the dominant photoreaction of the thio and seleno complexes, regardless of the nature of the absorption feature irradiated. For all degrees of photolysis, the ratio of the CT_1 to L_1 absorption maxima remained constant, and the ratio ϕ_r/ϕ_d was unity within our experimental error of about 5%. In the case of CoSN, Folin's test [9] showed detectable disulfides in irradiated solutions, but no detectable free mercaptide. Upon deaeration, neither ϕ_d, ϕ_r, nor the result of Folin's test changed. Similarly, ϕ_d and ϕ_r were unchanged on deaeration in the cases of CoSeN and CoSeO. For all three complexes, the yield ϕ_d was independent of light intensity over a three–ten fold range and of concentration of starting complex over the range 5×10^{-5} to 5×10^{-4} *M*. In addition, we have preliminary results indicating that $Co(cn)_2(l\text{-cysteine})^{2+}$ shares the same pattern of photochemistry; also redox reaction is a constant, wavelength independent component of the photochemistry of $Co(NH_3)_5(SCN)^{2+}$ [10]. Both of these complexes have the low energy absorption feature.

By contrast, photolysis of the thioether complexes results primarily in aquation. The ratio ϕ_r/ϕ_d decreases with increasing wavelength of irradiation. The photoaquation products are identified as $(en)_2Co(H_2O)(H_2NCH_2CH_2SR)^{3+}$, where R = CH_3 or benzyl [11]. Again, ϕ_d was independent of light intensity, concentration in the range 10^{-4}–10^{-3} *M*, and deaeration.

The differences in photochemistry between the two classes of complexes can be rationalized in at least two ways. We may be observing a difference in the chemistry of excited states. Certainly, the presence of the long wavelength shoulder in the cases of CoSN, CoSeN, and CoSeO and its absence in the cases of the thioethers indicate some difference in excited state structure.

An alternative view is that the photochemistry is due to hot ground state reactions. It is at least coincidental that CoSN, CoSeN, and CoSeO show only redox decomposition as their thermal chemistry, and CoMeSN and COBzSN, primarily aquation [12]. That is, the photochemical and thermal reaction modes are essentially the same. As has been noted [13], a pattern of decreasing quantum yields with

TABLE I. Photochemistry of Co–S and Co–Se Bonded Complexes.

Complex	313 nm irradiation[a]		515 nm irradiation[a]		580 nm irradiation	
	ϕ_d	ϕ_r/ϕ_d	ϕ_d	ϕ_r/ϕ_d	ϕ_d	ϕ_r/ϕ_d
CoSN	1.77×10^{-3}	1.0	2.83×10^{-5}	1.0	$<10^{-5}$	1.0
CoMeSN	8.8×10^{-3}	0.15	7.55×10^{-5}	<0.02		
CoBzSN	7.8×10^{-4}	0.48	2.32×10^{-5}	<0.02		
CoSeN	3.53×10^{-2}	1.0	5.06×10^{-5}	1.0		
CoSeO	7.4×10^{-2}	1.0	5.0×10^{-3}	1.0	$<10^{-3}$	1.0

[a] Defined to ±5 nm with the use of blocking and interference filters. Irradiations were at 25 ± 1 °C in pH 2 aqueous solution. Ferrioxalate and reineckate actinometry were used (see Ref. 13).

increasing wavelength is consistent with the expectation that the more 'hot' the nascent ground state, the more likely it is to react before energy dissipation to the medium occurs.

Regardless of explanation, the qualitative difference that we observe between the photochemistry of our RS^- and RSe^- complexes and those of the thioether type, RSR′, probably carries over to analogues in which either R or the central metal ion is varied. We are examining possibly useful comparisons to the chemistry and biochemistry of cysteine and methionine complexes of cobalt, molybdenum, and iron.

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8 The method is a new and, we believe, useful one. It makes use of the ability of Co(II) to complex with polydentate ammines and then to oxidize readily to strongly absorbing μ-peroxo complexes (see G. M. McLendon and A. E. Martell, *Coord. Chem. Rev., 19,* 1 (1976)). One cm^3 of $10^{-3}M$ tetren (tetraethylenepentamine pentahydrochloride) and 1 cm^3 of pH 8.7 borate buffer are added to 1.5 cm^3 of photolyzed solution, all solutions being air saturated. The Co(II) concentration was calculated from the optical density at 308 nm, using an extinction coefficient of $1.22 \times 10^4 M^{-1}$ cm^{-1} (M. Zehnder and S. Fallab, *Helv. Chim. Acta, 57,* 1493 (1974)). The reference blank consisted of 1.5 cm^3 of photolyzed solution to which 1 cm^3 each of buffer solution and of $1 \times 10^{-3}M$ ethylenediamine tetracetate has been added.

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11 The one-ended product (N-bonded) was identified by consideration of its absorption spectrum, which is similar to that of $Co(NH_3)_5(H_2O)^{3+}$. It was separated by elution from a Sephadex SP-25 ion exchange chromatographic column by means of 0.3 *M* sodium borate, behaving as a tri-positive ion at low pH and as a di-positive ion at pH > 7. Over a period of days, a solution of this product reverts nearly quantitatively to the original thioether complex; alternatively, the same product may be obtained by thermal reaction of the original thioether complex at 60 °C for several hours.

12 From our observed spectral changes on heating solutions of the complexes, and from chromatographic and Co(II) analysis.

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