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Photocatalytic Systems.
LXI.* Photochemical Synthesis of Tungsten(IV) Complexes of the Type [W(OR)$_4$phen]

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Introduction

It is well known that irradiation into the ligand field bands of octacyano complexes of molybdenum(IV) and tungsten(IV) in alkaline solutions leads primarily to substitution of one cyanide ligand by water [1]. The photochemical primary reaction is followed by a number of secondary thermal steps, resulting in a loss of further 3 cyanide ligands connected with the formation of the stable final product $[M(CN)_4O(OH)]^{3-}$ [2, 3]. We have been able to propose a photocatalytic system based on photochemical generation of free cyanide from octacyanomolybdate(IV) and octacyanotungstate(IV) respectively [4, 5].

Besides photochemical investigations in aqueous solutions we have been interested in photolysis experiments in mixed solvents and in the presence of ligands other than water. Thus recently we have been able to show the formation of tetracyanobis(phenanthroline) molybdenum(IV) [6] by irradiation of octacyanomolybdate(IV) in methanol/water mixtures and in the presence of 1.10-phenanthroline (phen) (1):

$$[Mo(CN)_8]^{4-} + 2\ \text{phen} \xrightarrow[CH_3OH/H_2O]{h\nu/\Delta} [Mo(CN)_4(\text{phen})_2] + 4CN^- \qquad (1)$$

We wish to report here the completely distinguished photochemical behaviour of octacyanotungstate(IV) in alcohol/solvent mixtures in the presence of an excess of 1,10-phenanthroline.

Experimental

Tetrakis(tetraethylammonium)octacyanotungstate(IV) was irradiated in $CHCl_3/ROH$ (3:1; v, v) mixtures as described elsewhere [6]. The isolation, purification and characterization of photolysis products obtained was performed as described for $[Mo(CN)_8]^{4-}$ [6]. Data of elemental analyses are in agreement with calculated data. IR (UR 20, VEB Carl Zeiss, Jena) and UV/VIS spectra (Specord, VEB Carl Zeiss Jena) were recorded in the usual manner. Magnetic moments were estimated by the Gouy method at room temperature only.

Results and Discussion

Surprisingly, octacyanotungstate(IV) irradiated under comparable conditions as the appropriate molybdenum(IV) complex [6] gives in each case, instead of the expected cyano–phenanthroline mixed ligand complexes, tetraalkoxo derivatives according to the following stoichiometry (2):

TABLE I. Complex Characteristics.

Complex molecular weight	μ_{eff} (in B.M.) at 298 K	IR bands (in cm^{-1})			Elemental analysis in % (calc./found)			
		ν(W–O)	ν(C=C) and ν(C=N) phen ring vibrations		W	C	H	N
[W(OCH$_3$)$_4$phen] 488.08	1.72	650	1422	1525	37.68	39.35	4.09	5.74
					37.3	40.0	4.3	5.5
[W(OC$_2$H$_5$)$_4$phen] 544.12	1.68	645	1420	1525	33.80	44.13	5.15	5.15
					33.2	44.4	5.3	5.1
[W(OC$_3$H$_7$-n)$_4$phen] 600.16	1.70	647	1425	1520	30.65	48.00	6.00	4.67
					29.9	49.1	6.3	4.8
[W(OC$_4$H$_9$-n)$_4$phen] 656.20	1.58	652	1420	1525	28.03	51.23	6.70	4.27
					27.8	50.7	6.5	4.4

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$$[W(CN)_8]^{4-} + \text{phen} \xrightarrow[\text{CHCl}_3/\text{ROH}]{h\nu/\Delta} + [W(OR)_4(\text{phen})] + 8CN^- \qquad (2)$$

($R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9$)

The complexes prepared photochemically are microcrystalline products of dark colour (see Table I). They are stable in air and very soluble in DMSO at temperatures up to 300 K (at higher temperatures decomposition is observed). The complexes obtained are characterized by intensive CT transitions between 570 and 580 nm. It follows unambiguously from IR spectroscopic investigations that cyanide ligands are substituted completely because no absorptions are observed in the range between 1900 and 2200 cm^{-1}. Instead of these bands new transitions at 1520 cm^{-1} (coordinated phenanthroline [7]), 700–900 cm^{-1}, 1100–1250 cm^{-1} and 1400–1650 cm^{-1} (further phenanthroline absorptions [8, 9]) and at 645 cm^{-1} W–O valence band) are seen. Room temperature magnetic moments between 1.6–1.7 B.M. are in agreement with those expected for octahedral tungsten(IV) complexes [10, 11] under conditions of strong spin–orbit coupling.

Beside the surprising result of different photolysis pathways among homologous complex compounds (formation of eight-coordinate diamagnetic molybdenum complexes $[Mo(CN)_4(\text{phen})_2]$ on the one side and octahedral paramagnetic tungsten complexes $[W(OR)_4(\text{phen})]$ on the other) the photochemical generation of eight mol of free cyanide instead of four in the case of $[W(CN)_8]^{4-}$ is of special interest for photocatalytic reasons. Furthermore, the synthesis of mixed ligand complexes of this type can be achieved very easily. Further investigations concerning mechanistic and structural details are in preparation.

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