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Preparation and Thin-Layer Chromatography of *cis*-Dicyanobis(2,2′-bipyridine)ruthenium(II)[1]

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Received July 15, 1968

The dicyanobis(2,2′-bipyridine)ruthenium(II) complex is of interest both theoretically[3,4] and experimentally for its possible practical applications. It exhibits an intense charge-transfer luminescence in a rigid glass[3] at 77°K as well as in solution at room temperature. This property, coupled with its broad absorption spectrum, makes it a potential candidate as a wavelength shifter, a quantum counter, or a laser material. To obtain substantial amounts of the substance having a high degree of purity we present a simple, high-yield preparation and purification scheme for the compound as an alternative to the published method.[5] In addition several thin-layer chromatographic systems for evaluating the purity of the product are described. Ultraviolet–visible absorption spectra of the complex in different solvents are presented which may be used by others to characterize the compound, and evidence is given supporting a *cis* assignment of the configuration.

The new synthesis was guided by thin-layer chromatography. Having prior knowledge of the R_f values of the product we were able to determine within 30 min after beginning a pilot run that the reaction was proceeding satisfactorily even though approximately 2 days was required for completion. Chromatography also afforded rapid (~30 min) evaluation of the purity at every stage of the preparation. The results from thin-layer chromatography also suggested the fruitful column chromatographic scheme for purifying the compound.

Experimental Section

Chromatography.—Thin-layer adsorbents were E. Merck (Darmstadt) silica gel (GF-254) and alumina (GF-254). Thin-layer chromatographic layers were 0.25 mm thick prepared by a Brinkmann Model S-II spreader on glass plates (5 cm × 20 cm). Both unactivated (air dried for at least 48 hr) and activated (dried 30 min at 110°) plates were used. Sample application and ascending tank development were performed in a conventional manner.[6,7] All R_f values (see Table I) were estimated to the center of gravity of the spot. The spots were visible by their own colors or under 254-mμ mercury light due to the ultraviolet indicator in the adsorbent. The cyano complex was also visible under 365-mμ light owing to its intense red-orange luminescence.

Column chromatography was performed in a Fischer and Porter 0.9 × 15 cm column with all Teflon fittings. The alumina was activity 1, neutral grade, from M. Woelm Eschwege, Germany; silica gel was Mallinckrodt SilicAR.

Chemicals.—The methanol used in the synthesis was freshly distilled AR grade. Methanol for the spectroscopic study was Baker spectrophotometric grade. The N,N-dimethylformamide was Eastman "White Label," also freshly distilled. AR grade sodium cyanide was used. Oxalatobis(2,2′-bipyridine)ruthenium(II)–4-water was prepared by the method of Liu, Liu, and Bailar[8] except that the potassium pentachloroaquoruthenate(IV) was replaced by an equivalent amount of commercially available potassium hexachlororuthenate(IV), and the initial reaction mixture was heated for 2 hr instead of 1 hr. This product was not recrystallized but was chromatographically pure on silica gel plates developed with methanol.

Absorption Spectra and Analyses.—Absorption spectra were run in matched 1-cm quartz cells on a Cary Model 14 recording spectrophotometer.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of *cis*-Dicyanobis(2,2′-bipyridine)ruthenium(II).—One gram of sodium cyanide in 25 ml of water was poured into 1 g of oxalatobis(2,2′-bipyridine)ruthenium(II)–4-water dissolved in 100 ml of methanol. The solution was refluxed with stirring for a total of 16 hr over a 2-day period. During the course of the reaction the dark purple solution changed to an orange-red. The reaction was monitored on unactivated silica gel thin-layer chromatographic plates using methanol. After the reaction had proceeded for 0.5 hr, three components were resolvable: the parent oxalato complex which appeared as a dark purple crescent, an unidentified by-product(s) with an R_f of 0.00, and the product. The reaction was stopped when virtually all of the oxalato complex had reacted. After evaporation to dryness at room temperature, the residue was extracted with two 15-ml portions of boiling water, and the extracts were filtered hot leaving the product as bright red crystals on the filter. At this stage of purification there was no detectable starting material and only small amounts of the by-product. The solid was air dried, dissolved in 20 ml of boiling methanol, and treated with three successive 1-g portions of silica gel[9] followed by a 1-g portion of alumina. After each treatment the sample was filtered hot, and the adsorbent was washed with boiling methanol. This procedure removed all but traces of the by-product. The final volume of solution was brought to approximately 40 ml, passed through a 3-cm length of alumina in a chromatographic tube,[10] and finally passed through 3 cm of silica gel. In both cases the columns were washed with approximately 10 ml of methanol. By evaporation of the solution to dryness, 0.47 g of product was obtained. The complex was chromatographically pure as shown by using silica gel plates with methanol and alumina plates with methanol or methanol–chloroform (1:9, v/v). This material did not give reproducible C, H, and N analyses but could be converted to the chromatographically identical dihydrate (by recrystallization from boiling water) which gave satisfactory analyses.

Anal. Calcd for $Ru(CN)_2(C_{10}H_8N_2)_2 \cdot 2H_2O$: C, 52.68; H, 4.02; N, 16.76; Ru, 20.15. Found: C, 53.15; H, 3.86; N, 16.89; Ru, 20.14.

Results and Discussion

Table I shows the results of the chromatographic studies of the complexes produced in this work. Any solvent less polar than methanol (*e.g.*, 1-propanol) did not produce measurable R_f values. There is no sig-

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[1] Research sponsored by AFOSR(SRC)-OAR, USAF, Grant No. AFOSR-68-1342.

[2] National Science Foundation Fellow, 1966–1968.

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[5] A. A. Schilt, *J. Amer. Chem. Soc.*, **85**, 904 (1963).

[6] "Chromatography Solvents and Apparatus for TLC and CC," Bulletin BR 153-B, Brinkmann Instruments, Inc., Westbury, N. Y.

[7] E. Stahl, Ed., "Thin-Layer Chromatography," Springer-Verlag, New York, N. Y., 1965.

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[9] Since the first treatment removed most of the by-products, additional treatment should be unnecessary.

[10] The treatments with alumina did not appear to affect the purity of the final product and can probably be eliminated from the purification procedure.

Table I

Compound	Adsorbent	Solvent	R_f
cis-Dicyanobis(2,2′-bipyridine)ruthenium(II)–2-water	Silica gel	CH_3OH	0.24
	Alumina	CH_3OH	0.73
	Alumina	$CHCl_3$–CH_3OH (9:1, v/v)	0.38
Oxalatobis(2,2′-bipyridine)-ruthenium(II)–4-water	Silica gel	CH_3OH	~0.03

nificant difference between activated and unactivated plates, and the results in the table are the average of both sets of values and were reproducible to ±0.03 R_f unit or better. It should be pointed out that the oxalato complex behaved differently in the reaction mixture than in the pure form. The pure material streaked from the origin, while the reaction mixture produced a sharp crescent of material well resolved from the origin but with about the same R_f value. Occasional streaking of the cyano complex was noticed if the plates had not air dried long enough.

Several lines of evidence lead us to assign a *cis* configuration to the cyano complex. We summarize them briefly.

Thin-layer chromatography has been used to assign complexes as *cis* or *trans* by the general rule that *cis* complexes, owing to their permanent dipole moments, interact more strongly with adsorbents and hence exhibit smaller R_f values than corresponding *trans* isomers.[11] Unfortunately, to apply this method, it is necessary to have both species; however, because of the extreme differences in behavior of uncharged geometric isomers toward solvents of differing polarity,[11] it is proposed that the low molecular weight *trans*-dicyanobis(2,2′-bipyridine)ruthenium(II) complex should exhibit a measurable R_f in solvents less polar than methanol (*e.g.*, acetone, 1-propanol, or chloroform). The absence of measurable R_f's in such solvents is evidence supporting the *cis* assignment of the complex.

Since the reaction presented here is a replacement reaction in which oxalate is replaced by two cyanides, it is expected to be a stereospecific preparation which would produce the *cis* species.

The absorption spectra for the dihydrate cyano complex and the oxalato starting material are given in Figure 1 for methanol and N,N-dimethylformamide (DMF) solvents. The most conspicuous features of both sets of spectra are the prominent charge-transfer bands in the visible and near-ultraviolet regions and the rather extreme solvent shifts upon changing from methanol to DMF for each compound. The solvent shifts of the cyano complex are in the same direction and are of comparable magnitudes to the shifts for the oxalato complex. It is difficult to imagine a nonpolar *trans* complex which would have qualitatively the same charge-transfer absorption and the same solvent shifts (both direction and magnitude) as measured in the polar oxalato complex. In addition, we have measured the solution spectra of the tris(2,2′-bipyridine-ruthenium(II) ion and have found no close resemblances of its charge-transfer bands to those reported here; we have found negligible solvent shifts also. Thus the great similarity in the sets of spectra measured for the dicyano and oxalato complexes is evidence for a *cis* assignment in the cyano complex, since the oxalato complex can only assume a *cis* configuration.

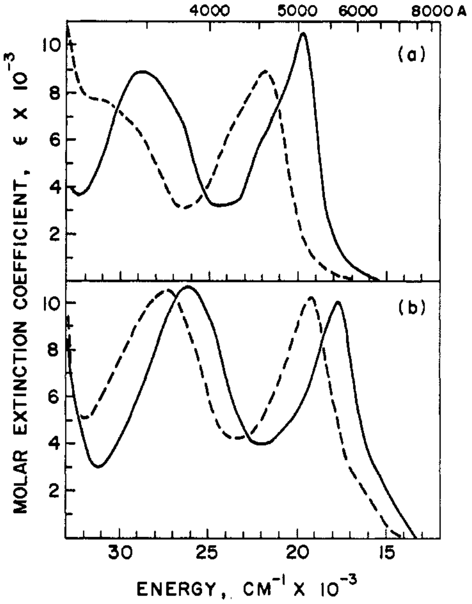

Figure 1.—Absorption spectra in methanol (- - -) and N,N-dimethylformamide (——) of (a) *cis*-dicyanobis(2,2′-bipyridine)-ruthenium(II)–2-water and (b) oxalatobis(2,2′-bipyridine)-ruthenium(II)–4-water.

As further evidence for a *cis* configuration we cite the work of Klassen,[12] who has made Kosower plots of the transition energy of the first charge-transfer band in the dicyano and the oxalato complexes *vs.* *Z* value, a measure of solvent polarity.[13] Solvents used were chloroform, DMF, acetonitrile, ethanol, methanol, and water. For both compounds good straight lines are obtained. Such behavior is just what is expected for molecules which undergo a change in dipole moment upon electronic excitation.[13] Since a centrosymmetric *trans* isomer does not possess a dipole moment in either the ground state or any excited state, a linear Kosower plot is strong evidence for a *cis* assignment.

In the preparation of the cyano complex given by Schilt[5] the author does not indicate whether his complex is *cis* or *trans*, although he has presented elsewhere infrared evidence which suggests a *cis* configuration.[14] We have compared the material prepared by Schilt's method with our preparation using thin-layer chromatography employing several solvent–adsorbent systems and have found the products to be identical. We infer that the method of Schilt also produces the *cis* isomer.

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