TABLE I

Experiment IV

Time of heating, hr.	Temp., °C.	Observed rotation	Yield in grams
50	70	−0.03	0.14
146	70	+0.04	0.16
		Experiment V	
48	73	−0.04	0.23
75[a]	73	+0.02	0.2

[a] In this case excess propylenediamine was added after 75 hours and the resulting solution was boiled to secure a more rapid displacement of the remaining tartrate ion. Excess calcium nitrate was subsequently added and the precipitated calcium *d*-tartrate removed by filtration.

on conditions and concentrations are being undertaken to achieve a more complete resolution.

At the present time the mechanism of this reaction is not fully understood. It was originally felt that the sole reaction was the one involved in the formation of the tris-levo-propylenediamine cobalt(III) chloride tartrate by the action of excess levo-propylenediamine on the tartrate complex according to the equation

$$[\mathrm{Co}(l\text{-pn})_2(\mathrm{tart})]\mathrm{Cl} + l\text{-pn} \longrightarrow [\mathrm{C\text{-}po}(l\mathrm{n})_3]\mathrm{Cl\ tart}$$

but it is now believed that additional reactions may occur also.

Experiment VI.—Further evidence that the two tartrato complexes have different stabilities was obtained by measuring the *p*H of aqueous solutions of the individual tartrato isomers containing excess levo-propylenediamine. The formation of the tris-propylenediamine complex is indicated by a gradual drop in the *p*H as propylenediamine molecules are removed from solution by coördination. A sample of each complex weighing 3.75 g. was dissolved in 9 ml. of water with subsequent addition of 9 ml. of 70% levo-propylenediamine. The solutions were then heated to 70°.

Time interval, hr.	*p*H of levo-tartrate solution	*p*H of dextro-tartrate solution
Zero	10.29	10.00
1	10.19	10.00
2	10.19	9.98
5	10.18	9.98
6	10.17	9.98
18	10.12	9.90
24	10.12	9.88
30	10.11	9.84
42	10.11	9.76
54	10.11	9.76
66	10.11	9.76
78	10.11	9.76
90	10.11	9.76

Here again it is seen that the complex containing the levo-tartrate ion appears to be less stable and undergoes a more rapid reaction than does the isomer containing the dextro-tartrate ion. Further efforts are being made to establish more precisely the differences in stabilities and reaction rates of these two isomers.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. IV

BY JAMES COLLINS, FRANCIS P. DWYER AND FRANCIS LIONS

RECEIVED OCTOBER 23, 1951

The base 1,8-diamino-3,6-dithiaoctane has been condensed with several different ortho-hydroxylated aromatic aldehydes to give Schiff bases which function as sexadentate chelate compounds. The coördination complexes derived from their combination with cobalt(III) ions show absorption minima between 540 and 580 mu. The cobalt(III) complex derived from *o*-vanillin has been resolved and appears to be suitable for rotatory dispersion studies.

It was pointed out in Part I[1] that the bis-salicylidene derivative of 1,8-diamino-3,6-dithiaoctane (EEE base) gave complex cobalt(III) salts when reacting with cobalt(II) salts in presence of oxidizing agents which showed maximum light transmission in 0.2% solution in 15% methanol of 65% at wave length 560 mμ. The relatively high molecular rotation of these optically active complex cobalt(III) salts suggests that despite their opacity they might prove of value in studies of rotatory dispersion. The present incomplete studies (which have had to be halted temporarily because of the transference of one of us (J. C.) to other work) were designed to prepare substances with greater optical transparency and more suitability for rotatory dispersion studies.

1,8-Diamino-3,6-dithiaoctane was condensed in hot ethanol with 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, 2-hydroxy-4-methylbenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde and 2-hydroxy-5-bromobenzaldehyde. Passage of air through a hot methanolic solution of any of the resulting Schiff bases containing cobalt(II) acetate led to formation of a cobalt(III) complex, the method being quite similar to that described for the bis-salicylidene complex described in Part I.[1]

All of these cobalt(III) salts had similar absorption curves (Figs. 1 and 2) showing in 0.2% solution a very steep rise in the transmission curve from about 20% at 400 mμ to about 85% at the maximum which lay between 540 and 580 mμ. Each of the substances showed an absorption maximum in the range 650–690 mμ and there was evidence that a weak absorption maximum existed at about 400 mμ, just outside the range of the recording spectrophotometer employed except for the complex derived from 5-bromosalicylaldehyde.

It was shown that the complex cobalt(III) ion derived from the Schiff base from *o*-vanillin exists in enantiomorphic forms by resolution through the *d*-antimonyl tartrates. The molecular rotations of the optically active iodides were found to be ±36,700°, for the sodium D line at 20°.

Experimental

1,8-Bis-(salicylideneamino)-3,6-dithiaoctanes.—These Schiff bases were readily prepared by admixture of hot methanolic solutions of 1,8-diamino-3,6-dithiaoctane (1 mole) and the substituted salicylaldehyde (2 moles) the yields be-

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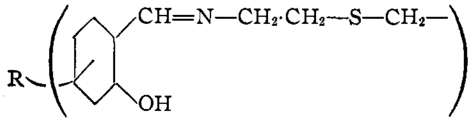
(1) F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950).

TABLE I

SUBSTITUTED 1,8-BIS-(SALICYLIDENEAMINO)-3,6-DITHIAOCTANES



R	Formula	Appearance	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
3-Methoxy-	$C_{22}H_{28}N_2O_4S_2$	Foliated needles	125–126	59.0	59.0	6.3	6.3	6.3	6.3
4-Methoxy-	$C_{22}H_{28}N_2O_4S_2$	Flat needles	87	59.0	58.9	6.3	6.3	6.3	6.3
5-Methoxy-	$C_{22}H_{28}N_2O_4S_2$	Needles	110	59.0	59.1	6.3	6.3	6.3	6.2
4-Methyl-	$C_{22}H_{28}N_2O_2S_2$	Needles	79	63.4	62.8	6.8	6.8	6.8	6.8
5-Nitro-	$C_{20}H_{22}N_4O_6S_2$	Needles	158–160	50.2	50.4	4.6	4.7	11.7	11.7
5-Bromo-	$C_{20}H_{22}N_2O_2S_2Br_2$	Needles	180	44.0	44.1	4.1	4.0	5.1	5.1

ing invariably good. The yellow crystalline products could be recrystallized from hot methanol and are listed in Table I.

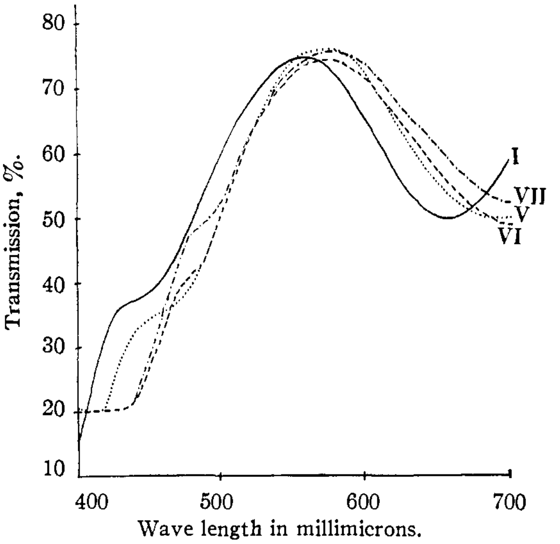


Fig. 1.—All measurements were made in a 1-cm. cell at 20°: I, 1,8-bis-(salicylideneamino)-3,6-dithiaoctane cobalt(III) chloride, 0.02% solution in water; II, 1,8-bis-(2′-hydroxy-5′-bromobenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide monohydrate, 0.02% solution in 25% aqueous methanol; III, 1,8-bis-(2′-hydroxy-4′-methylbenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide, 0.02% solution in 25% aqueous methanol; IV, 1,8-bis-(2′-hydroxy-5′-nitrobenzylideneamino)-3,6-dithiaoctane cobalt(III) bromide, 0.02% solution in 50% aqueous methanol.

Preparation of Cobalt(III) Complex Salts.—The method for the preparation of *dl*-1,8-bis-(2′-hydroxy-3′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide is described in detail. The other preparations were almost exactly similar. To a solution of 1,8-bis-(2′-hydroxy-3′-methoxybenzylidenamino)-3,6-dithiaoctane (1.5 g., 1 mole) in hot methanol (100 ml.) a hot methanolic solution of cobalt(II) acetate tetrahydrate (0.9 g., 1 mole) was added and the solution boiled for five minutes. Air was then drawn through the hot solution for 0.5 hour after which an equal volume of water was added and the aspiration of air continued for 4 hours. Excess 10% potassium iodide solution was then added to the green-brown solution and the resultant brown precipitate collected, taken up in hot water and caused to recrystallize by addition of a little potassium iodide. It came out in black needles, m.p. 220°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_4S_2)I$: Co, 9.3; I, 20.1. Found: Co, 9.4; I, 20.0.

***dl*-1,8-Bis-(2′-hydroxy-4′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide** was obtained in thick black prisms from aqueous potassium iodide solution, m.p. 222°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_4S_2)I$: Co, 9.3; I, 20.1. Found: Co, 9.3; I, 20.0.

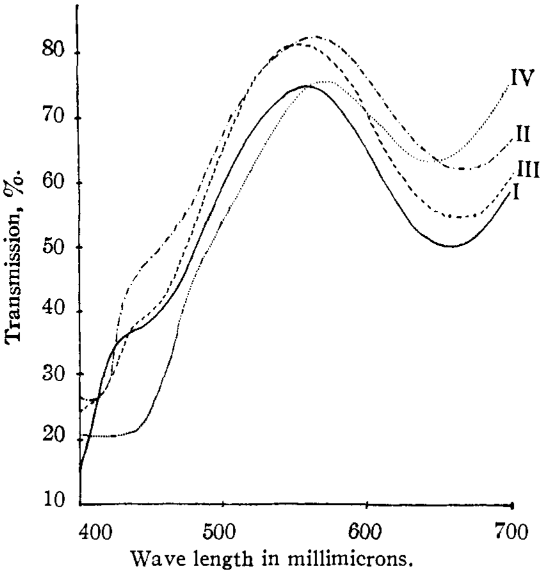


Fig. 2.—All measurements were made in a 1-cm. cell at 20°: V, 1,8-bis-(2′-hydroxy-3′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt (III) iodide, 0.02% solution in 25% aqueous methanol; VI, 1,8-bis-(2′-hydroxy-4′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide, 0.02% solution in 25% aqueous methanol; VII, 1,8-bis-(2′-hydroxy-5′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide, 0.02% solution in 50% aqueous methanol.

***dl*-1,8-Bis-(2′-hydroxy-5′-methoxybenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide** came out in black nodular prisms from aqueous potassium iodide solution. Its solution in water was dark green in color, m.p. 232°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_4S_2)I$: Co, 9.3; I, 20.1. Found: Co, 9.3; I, 20.2.

***dl*-1,8-Bis-(2′-hydroxy-4′-methylbenzylideneamino)-3,6-dithiaoctane cobalt(III) iodide** formed dark green triangular prisms, m.p. 248°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_2S_2)I$: Co, 9.8; I, 21.1. Found: Co, 9.7; I, 21.1.

***dl*-1,8-Bis-(2′-hydroxy-5′-nitrobenzylideneamino)-3,6-dithiaoctane cobalt(III) bromide** was obtained in thin green plates from the dark green aqueous solution. It decomposed before melting.

Anal. Calcd. for $Co(C_{20}H_{20}N_4O_6S_2)Br$: Co, 9.6; Br, 13.0. Found: Co, 9.6; Br, 12.9.

***dl*-1,8-Bis-(2′-hydroxy-5′-bromobenzylideneamino)-3,6-dithiaoctane Cobalt(III) Iodine Monohydrate.**—This very sparingly soluble salt crystallized from water in dark green or black prisms, m.p. 216°.

Anal. Calcd. for $Co(C_{20}H_{20}N_2O_2S_2Br_2)I \cdot H_2O$: Co, 7.9; I, 17.0. Found: Co, 7.8; I, 16.8.

***l*-1,8-Bis-(2′-hydroxy-3′-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) *d*-Antimonyl Tartrate Pentahydrate.**—The *dl*-iodide described above was suspended in water (150 ml.) and excess freshly precipitated silver chloride added. The mixture was then warmed to 50° and vigorously shaken for 20 minutes, after which the solids were filtered off and washed. The combined filtrate and washings (total volume 200 ml.) were then slowly treated with an almost saturated solution of potassium *d*-antimonyl tartrate (2.23 g.) in hot water, the sides of the container being scratched during the addition. Crystalline black prisms separated. These were collected and recrystallized several times from hot water to which a little potassium *d*-antimonyl tartrate was added. The final crystalline product charred on heating.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_4S_2)(C_4H_4O_7Sb)\cdot 5H_2O$: Co, 6.7; Sb, 13.8; H_2O, 10.2. Found: Co, 6.7; Sb, 13.7; H_2O, 10.3.

A 0.02% solution in water gave α_D −0.94° in a 1-dm. tube, whence $[\alpha]^{20}D$ −4,700°.

***l*-1,8-Bis-(2′-hydroxy-3′-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) Iodide Dihydrate.**—The *l*-complex *d*-antimonyl tartrate just described was suspended in water (2.5 g. in 100 ml.) at 40° and hydrochloric acid (5 *N*, 10 ml.) added. The mixture was then vigorously shaken until all the antimony had been precipitated as antimony oxychloride. After filtration, the green-brown solution of the active chloride was treated with potassium iodide. The precipitated active iodide was collected and recrystallized twice from hot water and obtained in black needles which sintered at 207° and melted at 212°.

Anal. Calcd. for $Co(C_{22}H_{26}N_2O_4S_2)I\cdot 2H_2O$: Co, 8.8; I, 19.0. Found: Co, 8.8; I, 19.1.

A 0.02% aqueous solution gave α_D −1.10° in a 1-dm. tube at 20°, whence, $[\alpha]^{20}D$ −5,500° and $[M]^{20}D$ −36,700°.

***d*-1,8-Bis-(2′-hydroxy-3′-methoxybenzylideneamino)-3,6-dithiaoctane Cobalt(III) Iodide Dihydrate.**—The filtrate left after precipitation of the *l*-complex *d*-antimonyl tartrate was strongly dextrorotatory (*vide supra*). It was precipitated fractionally with potassium iodide. The first (least soluble) fractions were mainly composed of *dl*-complex iodide. The more soluble fractions were rich in the *d*-complex iodide. They were collected and recrystallized many times from hot water to which potassium iodide was added until the specific rotation was constant. The black needles sintered at 207° and melted at 212°.

Anal. Found: Co, 8.9; I, 19.1.

A 0.02% aqueous solution gave α_D +1.10° in a 1-dm. tube at 20° whence, $[\alpha]^{20}D$ +5,500° and $[M]^{20}D$ +36,700°.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Intensities of Electronic Transitions of Acetylene in the Vacuum Ultraviolet[1]

BY GEORGE MOE[2] AND A. B. F. DUNCAN

RECEIVED SEPTEMBER 15, 1950

The absolute intensities of thirteen separate electronic transitions of acetylene in the region 1520–1050 Å. have been measured quantitatively. A one-meter vacuum grating spectrograph was used to photograph the spectrum. Molecular hydrogen lines occurring in this region from a low pressure hydrogen discharge tube were used as background for the absorption. Absorption coefficients were determined at wave lengths where these lines occurred, using the methods of photographic photometry. "Oscillator strengths" (*f*-numbers) for the transitions were found. The values obtained are compared with theoretical *f*-numbers calculated from approximate wave functions.

Introduction

The ultraviolet spectrum of acetylene has been the subject of numerous investigations. Early studies were confined to the region above 1800 Å. where some complex band systems were found between 2400 and 2000 Å.[3] The work was extended to the far ultraviolet by Price[4] and Price and Walsh.[5] The absorption between 2400 and 1500 Å. consists of many weak diffuse bands, the analysis of which is as yet unsatisfactory. From 1500 to 1050 Å., intense absorption bands representing fifteen electronic transitions were reported by Price,[4] who assigned the transitions to two Rydberg series. These series converge to the same ionization limit at about 92,000 cm.⁻¹.

The present investigation is directed primarily to the measurement of the intensities of these Rydberg series members. It was not possible with the equipment available to include the transitions at longer wave lengths in this work. Hence, only transitions between 1520 and 1050 Å. will be considered. The general theory of calculation of intensities of electronic transitions is discussed in detail in the report by Mulliken and Rieke.[6] The vector Q is

$$Q = \int \psi_k \sum_i r_i \psi_1 \, d\tau \qquad (1)$$

ψ_k and ψ_1 are the wave functions for the normal and excited electronic states, respectively. r_i is the radius vector of the i^{th} electron which enters into the transition. Transitions are either of the perpendicular type or the parallel type. In the former the electric moment moves perpendicular to the internuclear axis, which may be chosen to lie in the z direction. r then becomes either x or y. For parallel type transitions, $r = z$.

Theoretical Q^2's are compared with experimental *f*-numbers which are obtained in the following way. The absorption coefficient, α_ν, is determined at a large number of wave lengths within the absorption band. α_ν is defined by the equation

$$I_\nu/I_\nu^0 = e^{-\alpha_\nu l_0} \qquad (2)$$

where I_ν/I_ν^0 is the fraction of light of frequency ν(cm.⁻¹), transmitted by a column of gas of length l_0, measured in cm. at 0° and 76 cm. pressure. To obtain the total absorption strength for an entire electronic transition, α_ν is integrated over the

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[1] This work was supported in part under Contract No. N6onr-241, Task Order X with the Office of Naval Research, United States Navy.

[2] Part of dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] (a) S. C. Woo, T. K. Liu, T. C. Chu and W. Chih, *J. Chem. Phys.*, **6**, 240 (1938); (b) G. B. Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931); (c) G. Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

[4] W. C. Price, *Phys. Rev.*, **45**, 843 (1934); **47**, 444 (1935).

[5] W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

[6] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).