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Cambridge, Massachusetts 02139

Chromium Complexes of o,o'-Dihydroxyazo Dyes: Some Chemistry of 1:1 Complexes

By M. IDELSON, I. R. KARADY, B. H. MARK, D. O. RICKTER, and V. H. HOOPER

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Naphtholazo pyrazolone dyes were prepared and converted into 1:1 complexes with Cr(III); the 1:1 complexes were allowed to react with colorless ligands, such as β-diketones, amino acids, salicylaldehydes, polyamines, and tropolone. It was shown that the dyes coordinate to the chromium in the fac configuration. The effects of substituents on the spectra of the dyes are discussed.

Introduction

Chromium complexes of o,o'-dihydroxyazo dyes and o-carboxy-o'-hydroxyazo dyes are important commercial dyestuffs. The scientific investigation of their properties and constitution began many years ago. No attempt will be made here to review the field since several recent articles have adequately surveyed the literature.[1-4]

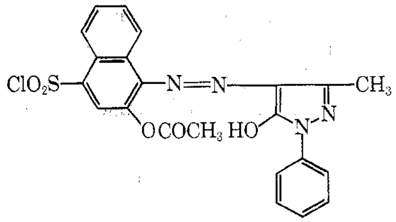
A number of aspects of dye–metal complexes are currently under investigation, each concerned with the more and more precise definition of the structure of the complexes. It was first established that o,o'-dihydroxyazo dyes are tridentate ligands.[5] In such a dye both hydroxyl groups and an azo nitrogen atom coordinate to the metal, usually copper, chromium, or cobalt. For copper this knowledge is sufficient to define precisely the structure of the square-planar complex, except as to which nitrogen atom coordinates in an unsymmetrical dye. For chromium(III) and cobalt(III) a new problem arises because of the octahedral arrangement of ligands around these metals. Drew[5] and Pfitzner[1] have discussed this situation at great length, and Grieb and Niggli have established the structure of one dye by X-ray diffraction.[6] The dye studied was a 2:1 chromium complex which was found to exist in the "perpendicular" or "Drew–Pfitzner" form as described in Schetty's work. In this structure the dyes occupy mer positions on the metal. Yagi[7] has been interested in the tautomeric form of the dyes, both free and as metal complexes. This work helps to determine which nitrogen atom coordinates with the metal. All of the structural work has been concerned with 2:1 dye–metal complexes with chromium and cobalt. While these complexes form the majority of the commercial metal complex dyes, the 1:1 complexes with chromium also constitute an important segment of the dye industry.

1:1 complexes with chromium became of paramount interest because of the clarity of their color in addition to the light stability characteristic of most metal complex dyes. Although this type of metal complex dye has been known and commercialized for many years, their chemistry has been neglected. This paper is an attempt to examine some of the chemical, physical, and optical properties of one class of these dyes.

Synthesis of Uncomplexed Dyes

While the dyes investigated all possess a characteristic basic structure, the peripheral modifications required several different modes of synthesis. The o,o'-dihydroxyazo dyes prepared are listed and assigned Roman numerals in Table II with the method used in the last column. Figure 1 gives the structure of the dye nucleus and shows the position of substituents, labeled X, Y, and Z. Table I gives the properties of dyes which served as precursors for dyes in Table II, and they are assigned lower case letters. The chromium complexes are listed and assigned Arabic numerals in Table III, which also refers by Roman numeral to the corresponding uncomplexed dye in Table II.

For those dyes in which the group X is cyano or sulfonic acid, the respective diazo oxides were coupled with the appropriate pyrazolone. This procedure is common in dye chemistry and will not be discussed here (see ref 8). 4-Sulfonamides of dyes containing the 3-methyl-1-phenyl-2-pyrazolin-5-one moiety were made *via* the sulfonyl chloride XX.[9]



XX

What might be termed nonconventional azo dye syntheses were applied in other cases. For example the dye I (Table II) was prepared in two ways. The first

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(1) H. Pfitzner, *Angew. Chem.*, **62**, 242 (1950).

(2) G. Schetty, *J. Soc. Dyers Colourists*, **71**, 706 (1955).

(3) G. Schetty, *Chimia* (Aarau), **18**, 244 (1964); *Am. Dyestuff Reptr.*, 589 (1965).

(4) G. Schetty and H. Ackermann, *Angew. Chem.*, **70**, 222 (1958).

(5) H. D. K. Drew and R. E. Fairbain, *J. Chem. Soc.*, 823 (1939).

(6) R. Grieb and A. Niggli, *Helv. Chim. Acta*, **48**, 317 (1965).

(7) Y. Yagi, *Bull. Chem. Soc. Japan*, **36**, 487, 493, 500, 506, 512 (1963); R. Jones, A. J. Ryan, S. Sternhill, and S. E. Wright, *Tetrahedron*, **19**, 1497 (1963).

(8) K. H. Saunders, "The Aromatic Diazo-compounds and their Technical Applications," 2nd ed, Edward Arnold and Co., London, 1949.

(9) M. Schmid and R. Mory, *Helv. Chim. Acta*, **38**, 1329 (1955).

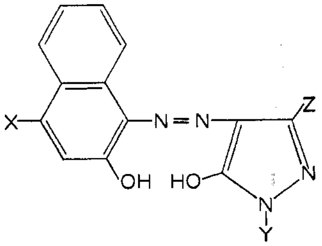
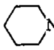


Figure 1.

TABLE I

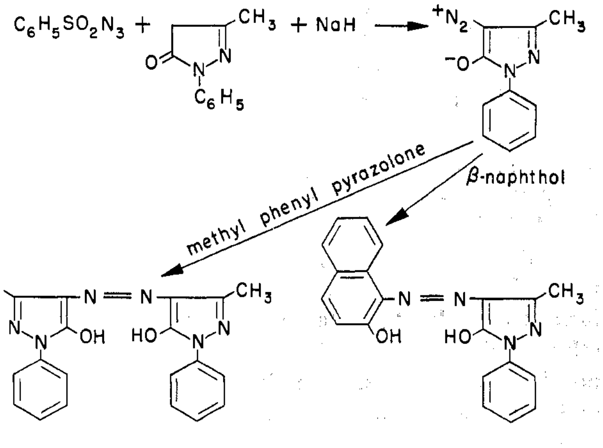
PROPERTIES OF NAPHTHALENEAZOPYRAZOLONE DYES[a]

Compd	X	Y	Z	Mp, °C	λ_{max}, mμ	$\epsilon \times 10^{-3}$
a	H	C_6H_5	CH_3	207–209	430	19.2
b	H	C_6H_5	$CO_2C_2H_5$	197–198	468	19.0
c	N—SO_2	C_6H_5	$CO_2C_2H_5$	223–225	448	22.6
d	$COCH_3$	C_6H_5	CH_3	219–221	430	23.4
e	$CH_3(n\text{-}C_4H_9)N\text{-}SO_2$	$m\text{-}C_6H_4NO_2$	CH_3	197–199	430	23.4
f	$CH_3(n\text{-}C_4H_9)N\text{-}SO_2$	$p\text{-}C_6H_4NO_2$	CH_3	233–234	426	26.0
g	H	C_6H_5	$NHCOCH_3$	257 dec	436	20.4
h	H	C_6H_5	NH_2	230–233	420	15.0

[a] The structure of these dyes corresponds to the general formula in Figure 1, but without the hydroxy group on the naphthalene ring.

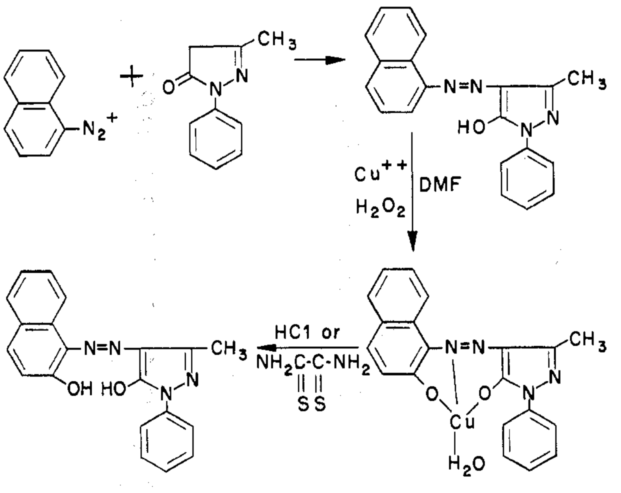
method, shown in Chart I, was used by Tedder and Webster to prepare symmetrical azo compounds.[10] By modifying their procedure we were able to obtain unsymmetrical dyes in low yield, with the symmetrical azo pyrazolones as the major product. A superior method is shown in Chart II.

CHART I



Oxidation of o-hydroxyazo dyes to o,o'-dihydroxy dyes by hydrogen peroxide and cupric ion has been known for some time.[11] Previous procedures called for vigorous conditions. For dyes of the class under investigation, however, it was found that nearly quantitative yields were obtained if the reaction were performed on the copper complex of the monohydroxy dye in DMF solution at −10 to 0°. The oxidation appears to be almost instantaneous. The success of this reaction depends on complete conversion of the starting dye into a 1:1 copper complex. If any dye forms 2:1 complex it is not oxidized at all; and if it is not complexed by copper it either is not oxidized or it is oxidized to the azoxy derivative.

CHART II



Removal of the copper from the complex was sometimes troublesome. Repeated precipitation into dilute hydrochloric acid was usually effective; stubborn compounds yielded to treatment with dithiooxamide in DMF. The copper complex of dithiooxamide was removed by filtration, and the dye was precipitated into dilute hydrochloric acid.

Over-all yields from 1-naphthylamine to o,o'-dihydroxyazo dye were as much as 80%. This method was used in cases where diazo oxides were not readily available.

Synthesis of 1:1 Chromium Complexes

The conditions under which an o,o'-dihydroxy- or o-carboxy-o'-hydroxyazo dye reacts to form a 1:1 complex were discovered by Drew and Fairbain.[5] Refluxing the dye in ethanol or water with excess chromic chloride hydrate until all the dye reacts gives, in every case we tried, a 1:1 complex, sometimes contaminated with a little 2:1 complex. The reaction mixtures were analyzed by paper electrophoresis (see the Experimental Section for the details).

Since most of the dyes studied did not contain acidic functions other than the groups *ortho* to azo, the 2:1 complexes with chromium(III) had a unit negative charge. The 1:1 complexes had different charges depending upon what the remaining three ligands were. When a 1:1 complex was prepared as described, the product often showed neutral and positively charged electrophoretic bands. The neutral fraction frequently hydrolyzed during the electrophoresis experiment to the positively charged species. It is believed that the reaction proceeds as follows.

$$\text{dye} + CrCl_3(aq) \longrightarrow [(\text{dye})Cr(H_2O)_3]^+ + [(\text{dye})Cr(H_2O)_2Cl]^0$$

The latter product hydrolyzes to the positively charged dye ion in the electrophoresis solvent. We call the above mixture the "chromic chloride" complex.

Synthesis of Mixed Complexes

We have observed that the chromic chloride complexes are not chemically stable. Under a wide variety

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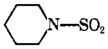
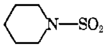
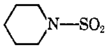
(10) J. M. Tedder and B. Webster, *J. Chem. Soc.*, 4417 (1960).

(11) H. Pfitzner and N. Baumann, *Angew. Chem.*, **70**, 232 (1958).

Table II

Properties of Naphtholazopyrazolone Dyes

Compd	X	Y	Z	Mp, °C.	λmax, mμ	ε × 10^{-3}	Method[a]
I	H	C_6H_5	CH_3	223–223.5	470	20.8	B, C (a)
II	H	C_6H_5	$CO_2C_2H_5$	175	500	28.8	B, C (b)
III	H	C_6H_5	$CONHCH_3$	230.5–232	493	21.4	D (II)
IV	CN	C_6H_5	CH_3	242–243	490	27.4	A
V	CN	C_6H_5	$CO_2C_2H_5$	240–241	500	28.8	A
VI	CN	C_6H_5	$CONHCH_3$	260	499	27.2	D (V)
VII	CN	C_6H_5	$NHCOCH_3$	258–259	480	27.6	A
VIII	CN	CH_3	CH_3	265.5–266.5	479	22.4	A
IX	CN	H	CH_3	255–256	475	21.0	A
X	CN	C_6H_5	NH_2	235–240	484		A
XI		C_6H_5	CH_3	236–238	476	24.8	D (XX)
XII	$(CH_3)_2NSO_2$	C_6H_5	CH_3	232–233	472	20.0	D (XX)
XIII		C_6H_5	$CO_2C_2H_5$	229–230	494	27.0	C (c)
XIV		C_6H_5	$CONHCH_3$	240.5–241	495	25.4	D (XIII)
XV	$CH_3(n\text{-}C_4H_9)NSO_2$	$m\text{-}C_6H_4NO_2$	CH_3	207–208	470	22.4	C (e)
XVI	$CH_3(n\text{-}C_4H_9)NSO_2$	$p\text{-}C_6H_4NO_2$	CH_3	208–210	475	22.8	C (f)
XVII	SO_3H	C_6H_5	CH_3		468	17.6	A
XVIII	$COCH_3$	C_6H_5	CH_3	206–207	476	17.3	C (d)
XIX	$CH_3(n\text{-}C_4H_9)NSO_2$[b]	$p\text{-}C_6H_4NH_2$	CH_3				
XX	$ClSO_2$	C_6H_5	CH_3	196–197			Ref 9

[a] A, diazo oxide coupled with pyrazolone; B, pyrazolone coupled with naphthol by toluenesulfonazide; C, oxidation of naphthalene azopyrazolone (compound in Table I); D, derived from precursor (compound number in Table II). [b] This dye was not prepared, but the chromium complex was made by catalytic reduction of **21**.

Table III

Properties of Chromium(III) Complexes

Compd	Parent dye	Ligand[a]	λ_{max_1}, mμ	λ_{max_2}, mμ	ϵ_1 × 10^{-3}	ϵ_2 × 10^{-3}
1	XVII		522	555	17.6	18.5
1	XVII	Na salt	514	539	15.0	13.9
2	XVII	acac	525	562	18.2	21.4
3	XVII	8-quinolinol	536	569	13.8	15.6
4	XII	acac	530	567	21.4	23.2
5	XII	dien	545	586	24.0	28.4
6	XII	$NH_2(CH_2)_2NHCH_2COOH$	537	577	23.2	26.4
7	IV	acac	537	575	22.0	24.6
8	IV	dien	549	591	20.6	25.4
9	IV	Cl	535	573	16.0	18.0
10	IV	Salicylic acid	539	576	22.4	23.0
11	V	acac	537	576	19.2	24.0
12	VI	acac	535	573	20.6	25.4
13[b]	VII	acac	546	585	21.4	22.6
14	VIII	acac	531	569	18.8	20.6
15	IX	acac	528	568	14.8	16.4
16	II	acac	520	556	16.8	20.4
17	III	acac	520	555	16.9	20.4
18[b]	XIII	acac	532	570	17.2	20.0
19	XIV	acac	533	570	19.4	23.4
20	XV	acac	530	567	20.0	21.6
21	XVI	acac	534	571	23.2	24.8
22	XIX	acac	533	568	20.7	20.9
23	IV	Tropolone	535	575	20.4	22.0
24[b]	XI	L-Proline	527	562	21.0	21.2
25	XII	Gentisaldehyde	531	566	21.9	20.4
26[b]	XI	Acetoacetanilide	527	563	17.4	18.0
27	XI	acac	524	556	21.4	22.0
28[c]	XVIII	acac	527	560		
29	I	acac	516	553	18.0	19.7

[a] Other than water. [b] Not obtained analytically pure. [c] Isolated from paper electrophoresis strips as the neutral fraction.

of conditions they either reverted to uncomplexed dye and Cr^{3+} ion or they formed the much more stable 2:1 complexes. As a rough generalization, *o*-carboxy-*o'*-hydroxyazo dyes formed much less stable 1:1 complexes than *o,o'*-dihydroxyazo dyes; the carboxy type complexes seemed to revert back to uncomplexed dye even though their 2:1 complexes are extremely stable. On the other hand, the dihydroxy type of 1:1 complex formed 2:1 complexes, which are also very stable. More will be said about this matter in the discussion of their stereochemistry.

A 1:1 complex consists of a tridentate, dibasic acid ligand coordinated to the chromium octahedron. The three remaining coordination positions would probably be reactive in displacement reactions with other ligands. We investigated the reactions of 1:1 complexes with amines, amino acids, β-diketones, salicylaldehydes, and hydroxy acids. The remaining coordination site in complexes containing a dye and a bidentate ligand would be satisfied by a water molecule.

Of the α-amino acids, only L-proline formed a complex which could be isolated. β-Aminobutyric acid formed a moderately stable product, but N-(β'-aminoethyl)-β-alanine (β-ethylenediaminopropionic acid) did not form a complex. On the other hand ethylenediaminemonoacetic acid readily formed a stable complex.

That L-proline formed an isolable complex while other α-amino acids, such as glycine, L-ornithine, L-arginine, L-lysine, and L-glutamic acid, failed can be explained by the fixed geometry of L-proline compared with the other α-amino acids. In other words, the pyrrolidine ring of L-proline fixes the positions of the α-nitrogen atom and the carboxyl oxygen atoms so that they are more readily complexed by the chromium atom; in addition the entropy of reaction will be more favorable for proline than for the open chain α-amino acids.

β-Diketones proved to be very useful as auxiliary ligands. 2,4-Pentane- and hexanediones, 2-acetylcyclopentanone, 2-acetylcyclohexanone, 1-methoxy-2,4-

pentanedione, and tri- and hexafluoro-2,4-pentanediones were some simple β-diketones which coordinated readily with the chromium atom. Salicylaldehydes, tropolones, and 8-hydroxyquinolines were further classes of ligands that formed stable dye complexes. Acetoacetanilide formed a less chemically stable complex while ethyl acetoacetate gave unclear results. The aliphatic hydroxy acids did not form complexes.

Polyamines form a slightly different but extremely useful class. Ethylenediamine (en) and diethylenetriamine (dien) have been found to react readily at room temperature with the chromic chloride complexes to give positively charged, water-soluble dyes. The dien complexes have proved to be especially valuable intermediates in the synthesis of many other dyes by displacement of the dien by another ligand.

We have found, for example, that the chromic chloride complex reacts with 2,4-pentanedione (acac) in ethanol at reflux to give a mixture of 2:1 complex, 1:1 dye–metal–acac complex, and unchromed dye. The chromic chloride complex, isolated by evaporation of the alcohol, reacted in hot dimethylformamide (DMF) with the diketone, but the product was a mixture of the mixed complex and 2:1 dye–metal complex. The dye–metal–dien complex reacted cleanly and quantitatively with the diketone in DMF to form the mixed complex of dye–metal–diketone. In some cases triethylamine was used to direct the reaction of the ethanol solution of the $CrCl_3$ complex to the desired product. What is probably a complex in which a triethylamine molecule has replaced a water molecule from the chromic chloride complex has been isolated in several cases. As these materials are extremely insoluble in solvents including DMF and dimethyl sulfoxide (DMSO), it has been difficult to procure analytically pure samples. Like the dien complexes, these compounds react readily in DMF with β-diketones to give the mixed complexes.

Stereochemistry

The stereochemistry of 2:1 complexes of dyes has been discussed thoroughly, and Schetty has conducted some elegant experimental work which has shed considerable light on this subject.[3] The X-ray diffraction study of Grieb and Niggli[6] has confirmed one of Schetty's conclusions, namely, that dyes that form a five- and a six-membered metal complex ring exist in the mer structure.

1:1 complexes have not been examined by the chromatographic technique because, whether a chromium complex exists in either the fac or the mer form, only one isomer is possible. (In this entire discussion, "isomer" is intended to mean a *dl* pair, whenever a racemate exists.) The introduction into a 1:1 complex of an auxiliary, colorless bidentate ligand does not change the general spectral properties of the dye and, therefore, probably does not change the stereochemistry. Figure 4 shows the spectrum of a chromic chloride complex and its acac and dien derivatives. A ligand such as 2,4-pentanedione incorporated into a complex introduces the possibility of three isomers, as shown in Figure 2 for the fac configuration, while the mer configuration offers only one possibility, shown in Figure 3.

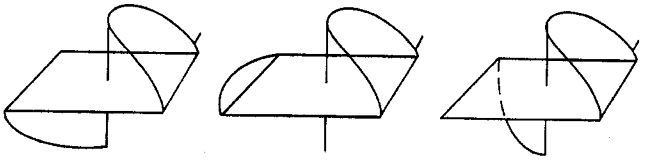


Figure 2.—*o,o'*-Dihydroxyazo dye coordinated to a Cr octahedron in the fac configuration with a bidentate ligand. This configuration leads to three isomers, each of which exists as a DL pair.

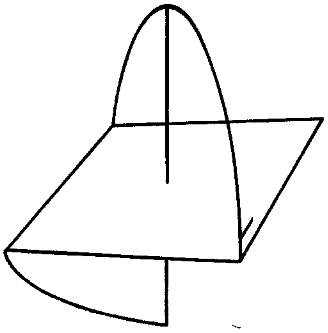


Figure 3.—*o,o'*-Dihydroxyazo dye coordinated to a Cr octahedron in the mer configuration with a bidentate ligand. This combination of ligands exists only as a DL pair.

The complex dye **27** was prepared and chromatographed on alumina.[12] It was separated into three bands by elutions with methylene chloride, acetone, and methanol–acetone. These fractions had identical infrared, visible, and ultraviolet spectra; their X-ray powder diagrams, however, were significantly different. We concluded that they must be isomers, and, therefore, the dye must be coordinated in a fac position on the chromium. One would expect different adsorptivity on alumina for such isomers because the sixth ligand position, which is occupied by a water molecule, would be more or less accessible to the alumina depending on its surroundings in the complex dye molecule.

Support for this conclusion could be obtained if a chromium compound were available in which there were two types of ligand, one of which was tridentate and occupied three fac positions, and the other monodentate, also necessarily in the fac form. A reaction between this compound and a dye molecule would probably result in the elimination of the three monodentate ligands if the dye assumed a fac position on the metal. A literature search revealed that $Cr(CO)_6$ reacts with dien at 160° to form $Cr(CO)_3(dien)$.[13] Abel, Bennett, and Wilkinson[13] concluded that the CO molecules are mutually perpendicular to each other, therefore occupying fac positions on the chromium. Here, then, is a compound satisfying the requirements set out above. No reactions for $Cr(CO)_3(dien)$ were reported, and in view of the conditions needed to prepare the compound, it seemed unlikely that it would be more reactive than $Cr(CO)_6$, which was totally inert toward dyes in reflux-

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[12] M. Idelson and I. R. Karady, *J. Am. Chem. Soc.*, **88**, 186 (1966).

[13] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

ing DMF. Nevertheless, $Cr(CO)_3(dien)$ was prepared and treated with the dye IV in DMF. A reaction occurred immediately at room temperature, giving the same product that was obtained from IV with $CrCl_3$ followed by treatment with dien. The ease with which these reactions occur and the fact that dien apparently prefers the fac configuration seem to indicate that the dye–Cr–dien complex is formed in both cases without internal rearrangement. The identity of the two dien complexes was established by their spectra and their reaction with 2,4-pentanedione.

The reaction between dye IV and $Cr(CO)_3(dien)$ is unusual in at least two respects. First, the conditions under which it was run are even milder than those used to displace a CO from $Cr(C_6H_6)(CO)_3$ by nitriles or amines[14] or from $Cr(dipy)(CO)_4$ by phosphites.[15] Second, these latter displacements involve no valence change in the chromium, but in the dye displacement reaction, Cr(0) is oxidized to Cr(III). This redox reaction is probably responsible for some failures in which the color of the dye was seen to fade rapidly instead of changing from orange to purple.

The existence of a fac structure for these 1:1 dyes is in conflict with the structure assigned by Schetty and by Grieb and Niggli,[6] but their assignments apply to 2:1 dye–metal complexes. It is not unreasonable that the structure changes on formation of 2:1 complexes, nor is it unreasonable that the structure of the complex is very sensitive to the dye structure. It was, in fact, shown by Schetty that relatively minor structural modifications could make dyes change their configuration in the 2:1 complex, and that some dyes could occupy either fac or mer sites depending on which were available.[10] While those dyes (which can exist in either fac or mer configuration) are all of the type that form two six-membered rings when complexed with a metal, the dyes reported in our study form a five- and a six-membered ring when complexed. It is not known whether our dyes in 2:1 complexes are mer or fac in structure. The fact that they are fac in 1:1 complexes does not preclude the mer form in 2:1 complexes. At this time it can only be stated with certainty that *o,o'*-dihydroxyazo dyes *are capable* of complexing in the fac form with chromium(III).

Spectral Properties of Dyes and Their Complexes

Figures 4 and 5 illustrate typical spectra of free dyes and complexes derived from them. These curves show the large bathochromic shift caused by complex formation and the splitting of the spectrum of the complex. An additional bathochromic shift caused by the dien ligand is also readily apparent.

By grouping the dyes in Table II in which X varies while Y and Z remain the same, we find three groups which show that X has essentially no effect on λ_{max}, with one exception. Systematic examination of the dyes in Tables II and III shows that the spectral behavior of the metal complex dyes is not related to the behavior of the uncomplexed dyes. Thus, λ_{max} of the free dyes is controlled more by the group Z than by the groups X or Y. On the other hand, λ_{max} of the chromium complexes is more sensitive to the group X than Y or Z. The effect of substituents on ϵ is parallel to the effect on λ_{max}. In other words, the group which affects λ_{max} also influences ϵ, except Y has virtually no effect on λ_{max} but ϵ decreases in going from aromatic to nonaromatic groups.

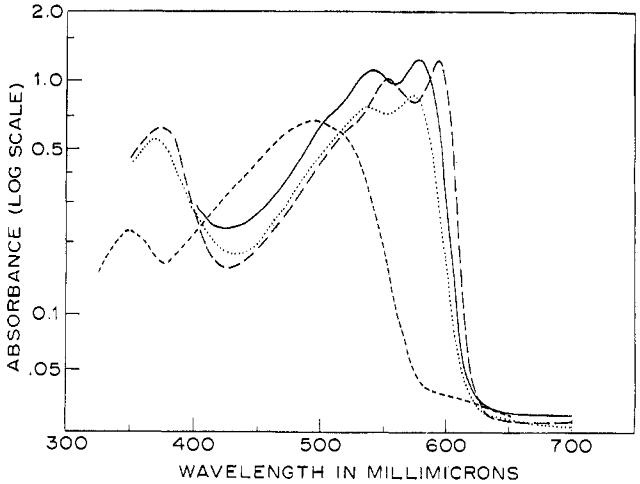

Figure 4.—The absorption spectra of: uncomplexed dye IV, – – – –; the chromic chloride complex **9**, · · · ·; the dien complex **8**, ——— ———; and the acac complex **7**, ———.

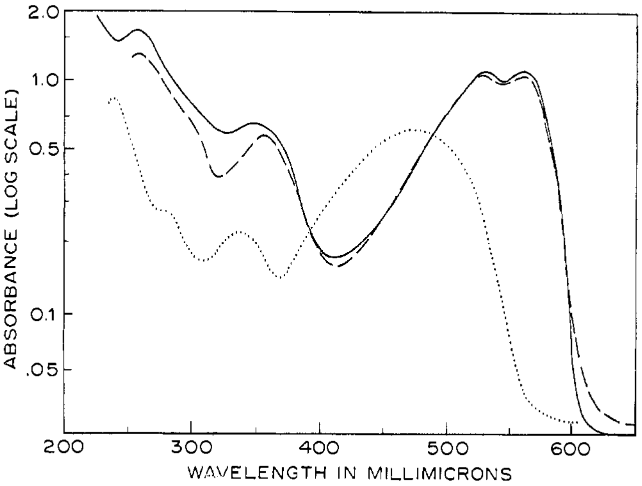

Figure 5.—The absorption spectra of: uncomplexed dye XI, · · · ·; the L-proline complex **24**, ——— ———; and the acac complex **27**, ———.

In examining the visible spectra we finally observe the effect of different ligands. The only generalization noted is that nitrogen-containing ligands, *e.g.*, dien and 8-quinolinol, cause a bathochromic shift when compared with oxygen ligands.

The ultraviolet region was studied by Yagi[7] in his examination of phenylazo–acetoacetanilide dyes. Without going into great detail, we have found general agreement with Yagi's results, the most significant being the relative insensitivity of the ultraviolet absorption to complex formation by the dye. Furthermore, ligands also have little effect on the ultraviolet

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(14) See, for example, W. Strohmeier and H. Hellman, *Z. Naturforsch.*, **18b**, 769, (1963).

(15) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).

absorption spectrum. These effects are illustrated in Figure 5.

We have examined numerous spectra of chromium complexes and have been able to assign certain bands to particular structural features in mixed complexes. The group of dyes in which β-diketones are present as a secondary ligand were studied most intensively.

We compared the infrared spectra of numerous mixed complexes containing β-diketones with the spectra of other complexes and with the spectrum of chromium(III) acetylacetonate ($Cr(acac)_3$). A typical set of spectra is shown in Figure 6. Chromium acetylacetonate shows four strong bands at 1575, 1520, 1425, and 1380 cm^{-1}. All chromium complexes exhibited very strong absorption at 1425 cm^{-1}. Mixed complexes containing 2,4-pentanedione showed all bands characteristic of $Cr(acac)_3$, but some complexes, such as chromium(III) chloride complexes, also exhibited absorption at 1575 cm^{-1} as well as 1425 cm^{-1}. The most reliable band for pinpointing an acac mixed complex is the 1515–1520 cm^{-1} peak. We make no attempt to assign the bands to individual structural features, although the 1380 cm^{-1} absorption must be at least in part due to the methyl groups of $Cr(acac)_3$.

The magnetic susceptibility of Inochrome Pink N (complex **1**) was found to be a normal 3.63 ± 0.15 BM.[16]

Experimental Section

Analytical Methods. (A) **Electrophoresis.**—Routine analyses were performed by paper electrophoresis in a Durrum type electrophoresis chamber constructed of CR-39 resin (Cast Optics Corp., Hackensack, N. J.). The buffer was prepared by adding 80 ml of 1 M KH_2PO_4 to 1 l. of 50% DMF–water. This system was used because almost all the dyes investigated are insoluble in water. The pH measured with a glass electrode of the above solution is 6.2. In practice this solution is alkaline enough to partially ionize phenols, naphthols, and N-alkylsulfonamides. Carboxylic acids and sulfonic acids act as though they are completely ionized.

Samples were applied from DMF solution, and the electrophoresis was carried out at 500 v. Separations required 0.5 hr, except those samples which contained several components of like charge. These materials usually separated (by chromatography on the paper during the electrophoresis run) in 1.5–2 hr.

(B) **Spectra.**—All visible and ultraviolet spectra were measured on Cary Model 10 and 11 recording spectrophotometers in 2-methoxyethanol at a concentration of 5×10^{-5} M in 1-cm cells. Infrared spectra were measured in KBr disks on a Perkin-Elmer Model 237 infrared recording spectrophotometer.

(C).—The results of elementary analyses are given for compounds whose actual synthesis is described. The analyses of most of the remaining dyes are shown in Tables IV and V. The compound numbers in Tables IV and V correspond wih those in Tables I–III.

Synthesis of Dyes. (A) **1-Phenyl-3-methyl-4-(4′-chlorosulfonyl-2′-acetoxynaphthalene-1′)azopyrazolin-5-one (XX).**—This is a modification of the method of Schmid and Mory.[9] A mixture of 100 g of Superchrome Red ECB (National Aniline) (XVII), 1000 ml of ethyl acetate, 100 ml of isopropenyl acetate, and 12 ml of concentrated sulfuric acid was stirred for 1.5 hr. Phosphorus pentachloride, 100 g, was added and refluxed with stirring an additional 2 hr. The reaction mixture was cooled and filtered. The solid was extracted thoroughly in a Soxhlet extractor with ethyl acetate. The product, XX (45 g, 50% if the dye were pure), crystallized from the solvent, mp 199–200°. Schmid and Mory give 206–207° from trichloroethylene.[9]

(B) **1-Phenyl-3-methyl-4-(4′-N,N-dimethylsulfonamido-2′-naphthol-1′)azopyrazolin-5-one (XII).**—Sulfonyl chloride XX, 10 g, was dissolved in 50 ml of 25% aqueous dimethylamine and warmed to 50° for 0.5 hr. The solution was poured into enough dilute HCl to neutralize the amine; the solid was collected and washed with water. The dried solid was stirred with 50 ml of

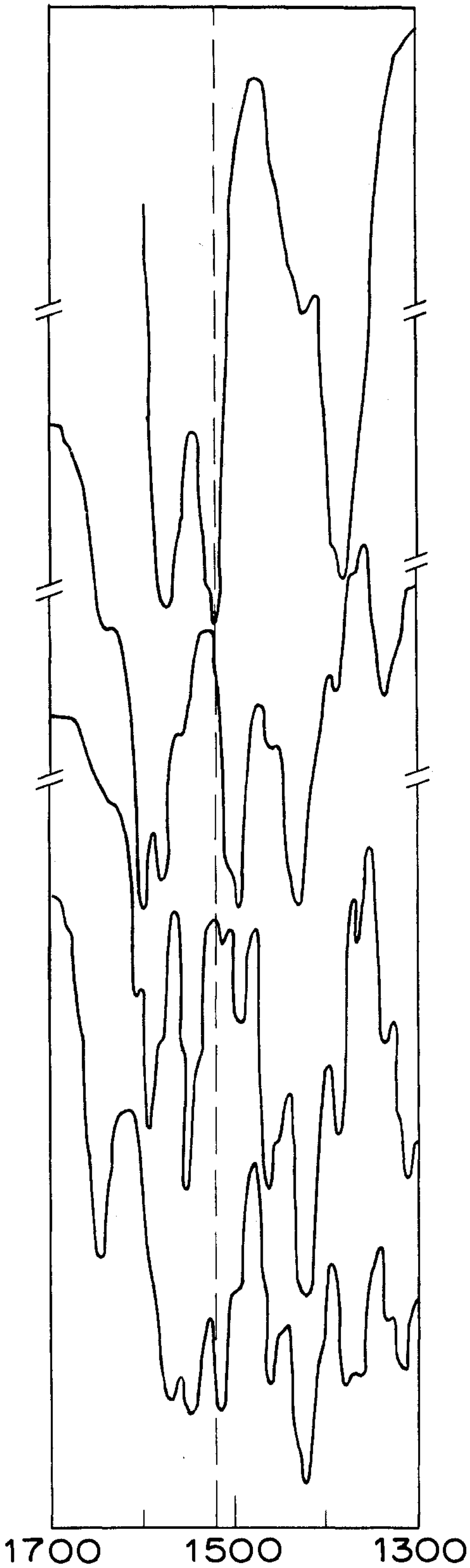

Figure 6.—From the top down the infrared spectra of $Cr(acac)_3$, chromic chloride complex **9**, dien complex **8**, and acac complex **7**.

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[16] F. A. Cotton, private communication.

TABLE IV

ELEMENTARY ANALYSES OF DYES

		C, %		H, %		N, %		S, %	
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
a	$C_{20}H_{16}N_4O$	73.20	73.38	4.88	5.00	17.08	17.20		
b	$C_{22}H_{19}N_4O_3$	68.30	68.00	4.91	4.9	14.47	14.3		
c	$C_{27}H_{27}N_5O_6S$	60.8	60.61	5.10	5.26	13.20	13.04	6.00	5.94
d	$C_{22}H_{18}N_4O_2$	71.40	71.3	4.60	4.8	15.1	15.3		
e	$C_{25}H_{25}N_5O_3S$	57.48	58.25	4.98	5.20	16.05	15.88	6.13	6.56
g	$C_{21}H_{17}N_5O_2$	68.0	67.87	4.58	4.71	18.85	19.04		
h	$C_{19}H_{15}N_5O$					21.3	21.5		
II	$C_{22}H_{18}N_4O_4$	65.66	65.63	4.51	4.67	13.92	13.81		
III	$C_{21}H_{17}N_5O_3$	65.04	64.85	4.38	4.60	18.08	18.10		
IV	$C_{21}H_{15}N_5O_2$	68.40	68.35	4.06	3.94	18.95	18.79		
VII	$C_{22}H_{16}N_6O_3$	64.1	63.9	3.89	4.00	20.4	20.24		
VIII	$C_{16}H_{13}N_5O_2$	62.5	62.31	4.24	4.59	22.8	22.69		
IX	$C_{15}H_{11}N_5O_2$	61.50	62.00	3.75	3.90	24.90	22.60		
XI	$C_{25}H_{25}N_5O_4S$	61.00	61.03	5.09	5.25	14.20	14.10	6.51	6.70
XIII	$C_{27}H_{27}N_5O_6S$	59.0	58.95	4.95	4.93	12.8	12.64	5.83	5.72
XIV	$C_{26}H_{26}N_6O_5S$	58.4	58.63	4.90	4.91	15.8	15.66	6.00	5.86
XVIII	$C_{22}H_{18}N_4O_3$	69.50	68.50	8.67	8.71	14.50	14.78		

TABLE V

ELEMENTARY ANALYSES OF CHROMIUM COMPLEXES

		C, %		H, %		Cr, %		N, %		S, %		
Compd	Formula	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Comments
1	$C_{20}H_{19}CrN_4O_8S$	45.55	44.76	3.61	3.95	9.86	9.81	10.62	10.81	6.08	6.26	
2	$C_{25}H_{23}CrN_4O_6S$	50.75	50.61	3.89	4.07	8.80	9.00	9.48	9.35	5.42	5.27	
5	$C_{26}H_{32}ClCrN_4O_6S$	49.30	48.14	6.05	6.00	7.11	7.32	15.31	15.45	4.38	4.32	($2C_2H_5OH$)
6	$C_{26}H_{28}CrN_7O_6S$	50.40	49.74	4.50	4.92	8.40	8.57	15.9	14.47	5.2	5.36	
7	$C_{29}H_{28}CrN_5O_6$	58.60	57.95	4.72	4.99	8.77	8.99	11.79	12.20	(% Cl)		*a*
8	$C_{25}H_{26}ClCrN_8O_2$	53.9	54.42	4.67	4.99	9.34	9.16	20.1	18.57	(6.28	5.72)	
11	$C_{28}H_{24}CrN_5O_7$	56.6	55.97	4.04	4.09	8.75	9.08	11.79	11.25			
12	$C_{30}H_{29}CrN_6O_7$	56.50	56.63	4.54	4.71	8.16	7.85	13.20	13.36			*a*
14	$C_{21}H_{20}CrN_5O_5$	53.15	52.90	4.22	4.51	10.98	10.73	14.76	14.65			
15	$C_{20}H_{18}CrN_5O_5$	43.65	43.59	5.10	4.84	9.45	9.22	12.71	12.45			($5H_2O$)
16	$C_{27}H_{25}CrN_4O_7$	57.00	56.73	4.39	4.37	9.13	9.40	9.84	9.66			
17	$C_{26}H_{24}CrN_5O_6$					9.38	9.21					
19	$C_{31}H_{34}CrN_6O_8S$	52.9	52.72	4.88	4.91	7.40	7.45	12.0	11.86	4.56	4.45	
20	$C_{30}H_{33}CrN_6O_9S$	51.10	51.39	4.68	4.80	7.37	7.55	11.90	11.75	4.54	4.60	
21	$C_{30}H_{33}CrN_6O_9S$	51.10	49.28	4.68	4.69	7.37	7.39	11.90	11.80	4.54	4.36	
22	$C_{30}H_{35}CrN_6O_7S$	51.80	52.20	5.30	5.47	7.48	7.32	12.10	10.56	4.60	4.49	(H_2O)
23	$C_{28}H_{20}CrN_5O_5$					9.31	9.25	12.51	12.65			
25	$C_{29}H_{26}CrN_5O_8S$	50.33	50.27	4.37	4.65	7.51	7.29	10.11	10.21	4.62	4.41	($2H_2O$)
29	$C_{26}H_{25}CrN_4O_5$	59.35	59.46	4.76	5.09	10.66	10.42	9.91	9.41			*b*

[a] $CH_3OCH_2CH_2OH$ instead of H_2O on Cr. [b] CH_3OH instead of H_2O on Cr.

boiling methanol, cooled, filtered, and washed with methanol. The melting point of this material was 229–231°; analytically pure XII (from Methyl Cellosolve) has mp 232–233°.

Anal. Calcd for $C_{22}H_{21}N_5O_4S$: C, 58.5; H, 4.7; N, 15.5; S, 7.1. Found: C, 58.23; H, 4.90; N, 15.24; S, 6.98.

Other sulfonamides were prepared similarly.

(C) **1-*p*-Nitrophenyl-3-methyl-4-(4′-N-*n*-butyl-N-methylsulfonamido-2′-naphthol-1′)azopyrazolin-5-one (XVI).** (a) **4-N-Methyl-N-*n*-butyl-sulfonamido-1-naphthylamine Hydrochloride.**—This amine was prepared from naphthionic acid sodium salt by (1) acetylation,[17] (2) conversion to the sulfonyl chloride,[18] (3) reaction with amine, and (4) hydrolysis.

To a solution of 56.7 g (0.2 mole) of 4-chlorosulfonyl-N-1-naphthylacetamide[18] in 200 ml of pyridine was added 52.2 g (0.6 mole) of N-methyl-*n*-butylamine (Eastman Kodak Co.) over a period of 2 hr. The solution was stirred at room temperature for an additional 2.5 hr. Then slowly 450 ml of 6 *N* hydrochloric acid was added. The product separated as a granular solid, mp 122–124°, 57.1 g (85%). The analytical sample had mp 125–126° from ethanol.

Anal. Calcd for $C_{17}H_{22}N_2O_3$: C, 61.0; H, 6.6; N, 8.4; S, 9.6. Found: C, 61.18; H, 6.81; N, 8.25; S, 9.76.

The crude product was hydrolyzed in 1 l. of 5.2 *N* hydrochloric acid at reflux for 2 hr. After standing overnight, the solid was collected, washed with water, and dried under vacuum to constant weight, 50 g (90%), mp 171–173° (analytically pure 174–175°).

Anal. Calcd for $C_{15}H_{21}ClN_2O_4S$: C, 54.80; H, 6.44; Cl, 10.80; N, 8.51; S, 9.76. Found: C, 54.75; H, 6.28; Cl, 10.80; N, 8.70; S, 9.90.

(b) **1-*p*-Nitrophenyl-3-methylpyrazolin-5-one.**—*p*-Nitrophenylhydrazine (Eastman Kodak Co.) (30 g, 0.2 mole) and 26.0 g (0.2 mole) of ethyl acetoacetate were heated together on a steam bath for 15 hr. To the resulting solid mass was added 25 ml of ethanol, and this was refluxed 1 hr. The product was ground with an additional 20 ml of ethanol and the product collected, 40.6 g (92.7%), mp 222–223°, lit.[19] 211–212°.

Anal. Calcd for $C_{10}H_9N_3O_3$: C, 54.8; H, 4.15; N, 19.2. Found: C, 54.6; H, 4.2; N, 19.2.

(c) **1-*p*-Nitrophenyl-3-methyl-4-(4′-N-*n*-butyl-N-methylsulfonamidonaphthalene-1′)azopyrazolin-5-one (g).**—To a mixture of 25 g (0.076 mole) of 4-N-*n*-butyl-N-methylsulfonamido-1-

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(17) G. Schroeter, *Ber.*, **39**, 1564 (1906).

(18) H. Schweitzer and K. Burr, U. S. Patent 1,939,025 (Dec 12, 1933).

(19) G. D. Padva, *et al.*, *Zh. Obshch. Khim.*, **27**, 2578 (1957).

naphthylamine hydrochloride and 250 ml of DMF was added 8.3 g (0.095 mole) of sodium bicarbonate in 20 ml of water and 5.25 g (0.076 mole) of sodium nitrite in 10 ml of water. The resulting slurry was slowly added to 350 ml of 1.2 *N* hydrochloric acid at 0°. The diazo salt is an orange solid. The diazo salt slurry was added to 16.4 g (0.076 mole) of 1-*p*-nitrophenyl-3-methylpyrazolin-5-one in 775 ml of DMF containing 10 g of sodium bicarbonate. The product, which is filtered better by gravity than with suction, was collected, washed with 1 l. of 3 *N* sulfuric acid and then with 1 l. of water, and dried under vacuum at 50°. The dye was stirred with 1 l. of boiling acetone, filtered hot, and dried, giving golden yellow flakes, 29.4 g (74%), mp 234–235°.

Anal. Calcd for $C_{25}H_{26}N_6O_5S$: C, 57.5; H, 4.98; N, 16.10; S, 6.13. Found: C, 57.36; H, 4.98; N, 15.94; S, 6.44.

(d) **Oxidation of g to XVI.**—(The yield from this reaction was poorer than for other compounds made by this method.) A filtered solution of 14.2 g (0.025 mole) of g and 9 g of cupric acetate in 750 ml of DMF was cooled to −10°. Slowly with external cooling, 9.3 ml of 30% hydrogen peroxide was added so that the temperature did not rise over 2°; it was stirred at 10° for 1 hr, then 100 ml of concentrated hydrochloric acid was added and the mixture was poured into 2.4 l. of 2 *N* hydrochloric acid. The solid was collected, dried, and dissolved in 750 ml of DMF. The treatment with hydrochloric acid was repeated as before. The yield was 8.6 g (60%), mp 208–210°. An analytical sample was obtained by crystallization from ethyl acetate, mp 216–217°.

Anal. Calcd for $C_{25}H_{26}N_6O_6S$: C, 55.60; H, 4.82; N, 15.59; S, 5.95. Found: C, 55.41; H, 4.98; N, 15.21; S, 7.22.

(D) **1-Phenyl-3-methyl-4-(2'-naphthol-1')azopyrazolin-5-one (I).**—In a 500-ml three-neck flask equipped with nitrogen inlet and a magnetic stirrer was placed 200 ml of dried tetrahydrofuran (THF) and 8.7 g (0.05 mole) of 1-phenyl-3-methylpyrazolin-5-one. In small portions 2.4 g (0.05 mole) of sodium hydride (dispersed in oil, Metal Hydrides) was added while flushing with nitrogen. It was stirred until all the hydride reacted.

In a 500-ml beaker was placed 9.85 g (0.05 mole) of *p*-toluenesulfonazide[10] and 50 ml of THF, and it was cooled to 0°. While keeping the pyrazolone solution under nitrogen at all times, it was transferred to a dropping funnel and slowly added to the azide solution with continual stirring. After an additional 10 min the wine red diazonium solution, which was no longer air sensitive, was transferred to another dropping funnel and slowly added to 7.2 g (0.05 mole) of 2-naphthol in 100 ml of THF. After stirring 1 hr, 3 l. of hexane was added, and the solid was collected, dissolved in water, and acidified with hydrochloric acid. The resulting product was crystallized from chloroform to mp 223–223.5°. The yield was about 1 g (6%).

Anal. Calcd for $C_{20}H_{16}N_4O_2$: C, 69.95; H, 4.68; N, 16.27. Found: C, 70.68; H, 4.89; N, 16.27.

(E) **1-Phenyl-3-ethoxycarbonyl-4-(4'-cyano-2'-naphthol-1')-azopyrazolin-5-one (V).**—4-Cyano-1-diazo-2-naphthol[20] (1.43 g, 0.0073 mole), 1.70 g (0.0073 mole) of 1-phenyl-3-ethoxycarbonylpyrazolin-5-one, and 0.8 g of sodum bicarbonate were stirred in 30 ml of ethanol for 2 hr. The solution was precipitated into 100 ml of 1 *N* hydrochloric acid, and the dried product was crystallized from DMF; 2.0 g (64%), mp 240–241°.

Anal. Calcd for $C_{23}H_{17}N_5O_4$: C, 64.60; H, 3.98; N, 16.40. Found: C, 64.60; H, 4.16; N, 16.60.

(F) **1-Phenyl-3-N-methylcarbamyl-4-(4'-cyano-2'-naphthol-1')-azopyrazolin-5-one (VI).**—Compound V, 1.0 g, was heated with 20 ml of 40% methylamine on the steam bath for 1 hr. The product was precipitated into dilute hydrochloric acid, and the dried material was crystallized from a mixture of methoxyethanol and DMF; 0.5 g (53%), mp 260° dec.

Anal. Calcd for $C_{22}H_{16}N_6O_3$: C, 64.1; H, 3.9; N, 20.4. Found: C, 64.12; H, 4.01; N, 20.28.

Chromium Complexes. (A) **Mixed Complex 4 by dien Route.**—The following series illustrates the preparation of a mixed complex using the dien mixed complex as an intermediate.

The chromic chloride complex was prepared by refluxing 1 g of XII with 1 g of $CrCl_3 \cdot 6H_2O$ in 35 ml of 95% ethanol for 6–10 hr. If any undissolved XII remained, more $CrCl_3 \cdot 6H_2O$ was added and refluxing continued. When all was dissolved, the composition was checked by paper electrophoresis. The mixture should contain no XII (orange anion) and no more than a trace of 2:1 complex (purple anion).

The cooled solution was filtered, 2 g of dien was added, and the mixture was allowed to stand at room temperature until all the chromic chloride complex reacted with the amine (about 0.5 hr), as shown by paper electrophoresis. The dien complex **5** is a cation. The complex **5** crystallized very slowly over a period of several days in the refrigerator, when it was collected and dried. The yield was 70–80% in several runs.

A solution of 2.0 g of dien complex **5** in 20 ml of DMF was refluxed for 5 min with 2.0 ml of acac and then precipitated into dilute HCl. The filtered and dried solid weighed 1.9 g (100%) and showed on electrophoresis the desired neutral product and only a faint trace of 2:1 complex.

(B) **Another Route to 4 Utilizing Triethylamine as a "Catalyst."**—The chromic chloride complex from 0.5 g (0.0011 mole) of XII and 0.5 g of $CrCl_3 \cdot 6H_2O$ in 20 ml of ethanol was heated with 16 ml of triethylamine and 0.11 g (0.0011 mole) of 2,4-pentanedione at reflux for 0.5 hr. Precipitation into dilute HCl and washing the product with methanol gave 0.3 g (48%) of mixed complex **4**.

Anal. Calcd for $C_{27}H_{28}CrN_5O_7S$: C, 52.4; H, 4.53; Cr, 8.4; N, 11.3; S, 5.18. Found: C, 52.35; H, 4.71; Cr, 8.27; N, 11.37; S, 5.06.

This latter route is more convenient than the dien route, but less general in scope. Reactive ligands, *e.g.*, 2,4-pentanedione and tropolone, work well by this method, but less reactive ligands, *e.g.*, acetoacetanilide, require the dien route.

(C) **Preparation and Separation of Mixed Complex 27 Isomers.**[12]—The commercial dye Inochrome Pink N[21] (1), 20 g, was stirred with 100 ml of methylene chloride and 10 ml of DMF in a flask equipped with a gas inlet tube which passed gas over the liquid, a condenser, and a mechanical stirrer. Phosgene was admitted for 0.75 hr, causing an exothermic reaction. The solvent was evaporated, replaced with 100 ml of fresh methylene chloride, and evaporated again to remove most of the phosgene. Again 100 ml of methylene chloride was added, followed by 10 ml of ethanol to decompose the DMF–phosgene complex, and then by 30 ml of piperidine. The reaction was stirred for 1 hr and poured into 200 ml of water, and the orgnic solvent was evaporated. The solid was collected, dissolved in acetone, precipitated into water, and washed thoroughly, giving 10 g of crude sulfonpiperidide.

Two grams of the crude dye was refluxed in 10 ml of ethanol with 2 g of 2,4-pentanedione for 1.5 hr. The solution was precipitated into water acidified with a few drops of concentrated H_2SO_4; the solid was collected, washed with water, and dried.

A 1-in. diameter chromatography column was packed with 150 g of Woelm acid-washed alumina (activity 1), using acetone. The column was washed with benzene. A concentrated solution of 1.5 g of dye in methylene chloride was applied to the column. Elution with methylene chloride removed only a small amount of yellow impurity; 1:1 acetone–methylene chloride gave no product; elution with acetone formed two bands which were collected and crystallized. Methanol–acetone (1:9) provided a third component which also crystallized. No additional dye could be eluted with pure methanol. The total crystalline product amounted to 0.5 g (fraction 1 (acetone), 0.2 g; fraction II (acetone), 0.2 g; and fraction III (acetone–methanol), 0.1 g). Ultraviolet and visible spectral data are given in Table VI. The infrared spectra were superimposable.

Anal of fraction II. Calcd for $C_{30}H_{22}CrN_5O_7S$: C, 54.70; H, 4.90; Cr, 7.90; N, 10.63; S, 4.87. Found: C, 53.7; H, 5.16; Cr, 7.97; N, 10.93; S, 4.84.

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(20) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 539 (1944).

(21) We are indebted to Francolor, Inc., Woonsocket, R. I., for providing us with a sample of this dye which was analytically pure.

TABLE VI

SPECTRAL DATA

Fraction	λ_{max_1}, mμ	ϵ_1	λ_{max_2}, mμ	ϵ_2	λ_{max_3}, mμ	ϵ_3	λ_{max_4}, mμ	ϵ_4
I	256	31,800	348	12,800	524	21,400	556	22,000
II	256	32,400	348	13,000	524	21,600	556	22,400
III					522	22,000	556	22,600

X-Ray powder diagrams taken by Mr. E. Emerson of these laboratories indicated significant differences which were interpreted as due to different crystal structures. The combination of different chromatographic behavior and different crystal structure led us to the conclusion that these materials must be isomers.

(D) **Reaction of IV with** (dien)Cr(CO)$_3$.—At 30° 1 g of IV was slowly added to a stirred mixture of 1 g of (dien)Cr(CO)$_3$ in 20 ml of DMF. After 0.5 hr the mixture was precipitated into water. The solid was collected, washed with water, and dried. Analysis by paper electrophoresis showed a mixture of a cation (the desired product), two anions (unreacted IV and 2:1 complex), and a trace of a neutral dye.

The mixture (1.05 g) was separated on a Stubbings electrophoresis apparatus (Tauratron, Inc., Fogelsville, Pa.) specially constructed of CR-39 resin. The buffer system was 1:1 DMF–1-butanol containing 0.016 *M* lithium acetate and 0.016 *M* acetic acid. The sample was injected as a 10% solution in DMF at 2 ml/hr; the buffer flow rate allowed about 2 hr for separation at 700 v and 30 ma. The eluate samples were analyzed by paper electrophoresis, and the pure cationic samples were combined and evaporated. The residue was washed with water, centrifuged, and dried. Additional material was obtained from the supernatant liquid by making it strongly alkaline with NaOH, which precipitated the dye, and thorough washing with water. The total amount of dye was 0.25 g. The infrared and visible spectra of this material were the same as the spectra of compound **5** prepared from the chromic chloride complex.

(E) **Reduction of a Nitro Group in a Chromed Azo Dye** (**21**) **to Amine 22.**—The azo dye XVI was chromed by the triethylamine procedure described for dye XII (using chromic chloride, ethanol, triethylamine, and acetylacetone). A mixture of 5.2 g (0.0074 mole) of complex **21** and 150 ml of *p*-dioxane was hydrogenated using a teaspoonful of Raney nickel at 40 psi and room temperature for 3 hr. (It was found that 10% Pd on charcoal was ineffective.) Celite was added, the mixture was filtered, and the filtrate was poured into 1 l. of water. The dye was a fine suspension that was collected by slow filtration with fluted coarse paper. Vacuum drying at 50° gave 4.0 g (80%) of the amino compound **22**.

Anal. Calcd for $C_{30}H_{35}N_6O_7SCr \cdot H_2O$: C, 51.80; H, 5.30; Cr, 7.48; N, 12.11; S, 4.60. Found: C, 52.20; H, 5.47; Cr, 7.32; N, 10.56; S, 4.49.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

New Synthetic Studies on Four-Coordinate Complexes Derived from Bis(trifluoromethyl)-1,2-dithietene and Some Related Reactions

BY A. DAVISON, D. V. HOWE,[1a] AND E. T. SHAWL[1b]

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A new synthetic route to complexes derived from bis(trifluoromethyl)-1,2-dithietene is described. New complexes of Cu and Au have been characterized, and a more convenient synthesis of the known Co, Ni, Pd, and Pt species is reported. A novel five-coordinate gold complex $[(C_6H_5)_3P \cdot AuS_4C_4(CF_3)_4]Cl$ has also been characterized. The desulfurization reactions of the neutral $[MS_4C_4R_4]$ species by triphenylphosphine to give four-coordinate $\{[(C_6H_5)_3P]_2MS_2C_2(CF_3)_2\}$ with M = Ni, Pd, and Pt are discussed. Polarographic studies of the $[MS_4C_4R_4]_z$ complexes with M = Co, Ni, and Cu are discussed in terms of the various electronic structures which have been proposed for these species. Evidence is presented which shows that certain of the cobalt complexes should be correctly formulated as dimeric dianions, *e.g.*, $[N(C_4H_9)_4]_2[CoS_4C_4(CN)_4]_2$, rather than, as previously assumed, monomeric monoanions.

The discovery of discrete one-electron-transfer reactions for both the bis-[2a] and the tris-[2b](*cis*-1,2-disubstituted ethylene-1,2-dithiolato[3])metal complexes has led to a continued interest in these and related systems. Much of the recent work has shown the remarkable versatility of this ligand system. In the bis complexes of the nickel group metals, a planar array of the four donor atoms is maintained in three apparent oxidation states[3,4] of the system. A planar structure was also found[5] for a characterized[6a] four-coordinate complex of copper in an $S = 0$ ground state. Metal-to-sulfur bonding between essentially planar units has been found[7] for $[CoS_4C_4(CF_3)_4]_2$ which has the structure shown in Figure 1. In this dimeric species, the metal-to-sulfur

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(1) (a) NSF Student Participant, 1964; (b) Woodrow Wilson Fellow, 1964–1965; NSF Graduate Fellow, 1965–1967.

(2) (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); (b) *ibid.*, **86**, 2799 (1964).

(3) This nomenclature, adopted to simplify electron bookkeeping, restricts us to an apparent or formal oxidation state of the metal only in a pedantic sense. However, these complexes are highly covalent and should properly be described in molecular orbital language. The electrons in the uppermost levels are associated with both ligand and metal. The degree of delocalization depends upon the metal and the total charge on the complexes. Such ambiguity between the concept of valence state and oxidation state arises quite often in transition metal chemistry, indicating that in many cases the ionic model and the valence bond descriptions do not provide a reasonable approximation to the bonding in such complexes.

(4) There is well-documented evidence that all three members of the nickel electron-transfer series are planar: (a) $[NiS_4C_4(CN)_4]^{2-}$, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965); (b) $[NiS_4C_4(CN)_4]^-$, G. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966); (c) $NiS_4C_4(C_6H_5)_4$, D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

(5) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1507 (1964).

(6) (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **2**, 1227 (1963); (b) H. B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963), reported the first characterized $S = 0$ complex of copper.

(7) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).