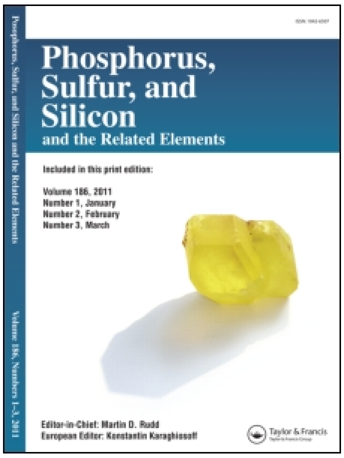

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Raymond F. X. Williams[a]
[a] Department of Chemistry, Howard University, Washington, D.C., U.S.A.

To cite this Article Williams, Raymond F. X.(1976) 'TRANSITION METAL COMPLEXES WITH ORGANO-CHALCOGEN LIGANDS. I. SYNTHESIS OF DITHIOCROCONATE DIANION', Phosphorus, Sulfur, and Silicon and the Related Elements, 2: 1, 141 — 146

To link to this Article: DOI: 10.1080/03086647608078939

URL: http://dx.doi.org/10.1080/03086647608078939

Phosphorus and Sulfur
1976, Vol. 2, pp. 141–146

TRANSITION METAL COMPLEXES WITH ORGANO-CHALCOGEN LIGANDS.
I. SYNTHESIS OF DITHIOCROCONATE DIANION

by

Raymond F. X. Williams

Department of Chemistry, Howard University, Washington, D.C. 20059, U.S.A.

(Received September 21, 1975)

ABSTRACT

A new sulfur containing oxocarbon derivative, the dipotassium salt of 1,2-dimercapto-3,4,5-cyclopentenetrione (potassium dithiocroconate) has been synthesized by reaction of dimethyl croconate with alcoholic potassium hydrogen sulfide. Solutions containing the dianion of this salt react to form intensely colored complexes of varying hues with several transition metal ions. Spectral and esr measurements on Ni(II) and Cu(II) indicate complexes with 2:1 ligand/metal ratio having dithiolene properties are formed in solution. Visible-uv and infrared studies suggest dithiocroconate dianion has less resonance stabilization than croconate dianion.

Introduction

Aromatic compounds with 1,2-dimercapto substitution on the ring system have been successfully employed in the synthesis of transition metal complexes with novel geometrical and electronic structural properties.[1] The effect of the electronegativity of substituents in the aromatic ring has been noted, and ligand systems with stronger electron-withdrawing substituents have been sought for some time. The synthesis of potassium salts of 1,2-dimercaptocyclobutenedione (dithiosquaric acid) and some transition metal complexes of this ligand were recently reported.[2] Preliminary structural data on the planar complex ion containing Ni(II) was also reported. Two features of interest are observed here—the "quinone" type oxygen substituent in the ring conjugated with the dithiolene grouping, and the degree of resonance stabilization possible in the dianionic ligand. The MS_4 coordination sphere reported in the planar complex, $[Ni(S_2C_4O_2)_2]^{2-}$, is noticeably distorted from the square geometry predominantly occurring in related Ni(II) complexes with unsaturated 1,2-dithiolene ligands.[3] This might be a combination of steric requirements in the four-member ring of the ligand, optimum M–S bond lengths in the Ni(II) chelates with 1,2-dithiolene ligands, and loss of some of the oxocarbon resonance stabilization by sulfur substitution and chelation.

Comparison of available structural data on oxocarbon dianions[4] and interpolation of typical M–S and C–S bond lengths observed in other *bis*-dithiolene complexes[3] suggested that a 1,2-dithiocroconate or 1,2-dithiorhodizonate would give nearly square MS_4 coordination spheres in a planar situation. Additional stability would be expected for the "regular" coordination site geometry and an increased number of electron withdrawing groups would be realized. Recognizing the great stability of the croconate dianion, initial efforts were made at introducing the sulfur donor atoms into this ligand. The synthesis of the potassium salt of 1,2-dimercapto-3,4,5-cyclopentenetrione (dithiocroconic acid) and characterization of this ligand is reported here.[5]

Experimental Section

Chemicals

Reagent grade chemicals obtained from Fisher Scientific Company were used throughout, except as noted. Absolute ethanol was obtained from local sources. Benzene and ethanol were dried by refluxing over sodium-lead alloy chips, followed by distillation. Hydrogen sulfide was obtained from Matheson Gas Products.

Physical Measurements

Electronic spectra were measured using a Beckman Acta III recording spectrophotometer, with distilled water as solvent, unless otherwise noted. Esr spectra were measured on a Varian E-9 spectrometer operating at 9.5 GHz using 100 KHz modulation. A Perkin-Elmer model 621 was employed for the infrared measurements. Elemental analyses were obtained from Galbraith Laboratories. Nmr spectra were obtained with the aid of a Varian EM-360 60 MHz spectrometer.

General

Moisture was excluded in the synthetic procedures by employing Kontes Glass Company Airless Ware system components in conjunction with locally fabricated pieces in a nitrogen atmosphere using methods described by Shriver.[6]

Potassium Croconate

Barium croconate monohydrate was prepared from myoinositol using minor modifications of the published procedure.[7] This material, 45 g, 0.15 mol, was added in portions to a stirred hot solution of K_2CO_3 (42 g, 0.284 mol) in 300 ml of water in a 1-liter flask. After boiling 12 minutes, the reaction mixture was filtered through a preheated pressure filter (Kontes Airless Ware). The reaction flask and filter were rinsed with three 25 ml portions of hot 7% K_2CO_3 solution. The filtrate was then neutralized in a large beaker by cautiously adding 60 ml acetic acid, followed by 40 ml water and 30 g $KC_2H_3O_2$. A precipitate of light yellow needles separated from the solution. The mixture was warmed to 90° to redissolve this material, then set aside to cool. Light yellow needles separated at higher temperatures followed by orange needles at lower temperatures, while the initial precipitate turned orange also. After 16 h, the mixture was further cooled in ice, filtered in a pressure filter, washed with two 50 ml portions of ice-cold 50% $KC_2H_3O_2$ solution, then twice with 95% ethanol, then dried by passing through a stream of nitrogen for 15 min. The orange precipitate underwent a slow transformation to yellow when dried *in vacuo* at room temperature. It was further dried *in vacuo* at 70° overnight. Yield: 28.2 g, 86% of theory.

Silver Croconate

Anhydrous potassium croconate, 35 g, 0.16 mol, was dissolved in 400 ml warm distilled water, and treated with a solution of silver nitrate (58.0 g, 0.34 mol) in 100 ml hot distilled water in a relatively darkened room. The orange precipitate which formed was separated from the chilled reaction mixture by filtration, washed 5 times with ice-cold water, then 95% ethanol, followed by methanol, and dried by suction, followed by further drying *in vacuo* at 75° for 12 h. The yield, 57.0 g, is essentially quantitative. Prolonged exposure to direct lighting was avoided.

Dimethyl Croconate

Silver croconate, 56.0 g, 0.157 mol, was treated with a solution of 40 ml methyl iodide (91.2 g, 0.638 mol) in 375 ml of dry benzene in an Airless Ware system under a nitrogen atmosphere using the Soxhlet extraction procedure described by Yamazaki.[8] The volume of the resulting orange solution was reduced by distillation to about 150 ml, and the remainder of the benzene sublimed to a trap cooled in dry ice-methanol at forepump pressure. The dry yellow product was not recrystallized or weighed, but was utilized directly in a later step.

Potassium Hydrogen Sulfide

Absolute ethanol, 250 ml, was allowed to react in a 500 ml Airless Ware flask with chunks of potassium metal (16.2 g, 0.414 mol) which had been cleaned under mineral oil. A gas dispersion tube and a magnetic stirring bar were inserted and the solution was saturated with dry hydrogen sulfide carried over in a stream of nitrogen over a four hour period by noting when gas absorption ceased. A quantity of white precipitate settled out. The excess hydrogen sulfide was removed by sparging the stirred mixture with nitrogen for 20 min. Addition of 135 ml dry ethanol produced a homogeneous solution, which was used immediately in the following step.

Potassium Dithiocroconate

The flasks containing dimethylcroconate and the KSH solution were connected with a right angle tube and the KSH transferred. A dark red mixture was formed with substantial quantities of suspended material. The transfer tube was removed and the first flask capped and shaken several minutes, then stirred two hours magnetically with intermittent shaking. The mixture was then cooled, filtered through a sintered glass funnel, then the reaction flask and the precipitate were rinsed three times with ethanol, dried by suction 15 min, then dried *in vacuo* at room temperature. The resulting dark red solid, 38.2 g, was recrystallized from 450 ml warm water by addition of 500 ml hot methanol to give 32.8 g maroon colored needles. The material was dried at 63° *in vacuo* and underwent a change in color to give very dark purple-red material. *Anal.* Calcd for $K_2C_5O_3S_2$: C, 23.99; S, 25.61. Found: C, 23.85 and 23.72; S, 25.39 and 25.13; H, 0.18 and 0.24.

Silver Dithiocroconate

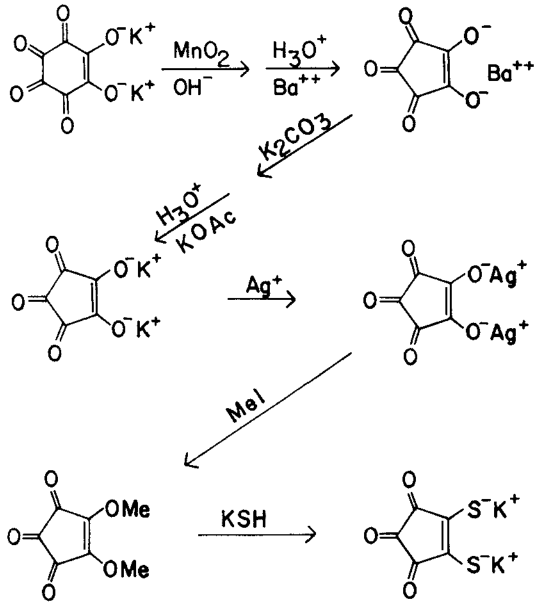
A solution of 0.57 g potassium dithiocroconate in 80 ml distilled water was treated with a 10% excess of silver nitrate solution. The deep red precipitate was collected, washed several times with water, then methanol, and dried *in vacuo* at 84° overnight. The dried material is dark red-black, and was analyzed for Ag by heating to 750° in a furnance and weighing the residue. *Anal.* Calcd for $Ag_2C_5O_3S_2$: Ag, 55.6. Found: Ag, 55.1.

1,2-bismethylthio-3,4,5-cyclopentenetrione

Dried silver dithiocroconate (380 mg) was suspended in 80 ml dried benzene, to which 5 ml methyl iodide was added. The mixture was stirred 72 h, filtered, and the benzene and excess methyl iodide were removed by freezing the mixture and subliming them to a cold trap at forepump pressure. The remaining red solid was dried 1 h *in vacuo* at 25°. nmr ($CDCl_3$) 3.07 ppm (s). No elemental analysis was carried out.

Results and Discussion

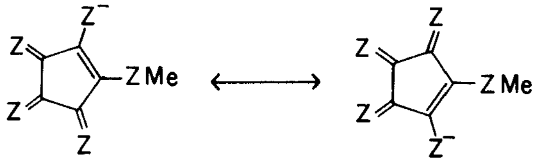
The method employed in the synthesis of potassium dithiocroconate (K_2dtcroc) is depicted in Scheme I. Analytical data cited above establish the formulation as $K_2C_5O_3S_2$, and the silver(I) derivative as $Ag_2C_5O_3S_2$. A reaction identical to that employed in the synthesis of well characterized dimethyl croconate[9] from silver croconate was carried out on the silver salt



SCHEME I

of dithiocroconate. The red solid obtained is soluble in methanol, chloroform, water, and benzene but insoluble in carbon tetrachloride. The nmr spectrum shows one singlet only, the visible-uv spectrum in acetonitrile is similar to that of K_2dtcroc in 10^{-1} M perchloric acid solution (*vide infra*), and the ir spectrum shows strong bands at 1752, 1714, and 1673 cm^{-1}.

The canonical structures for two possible formulations of the $C_5O_3S_2{}^{2-}$ ion (1,2- or 1,3-dimercapto) have negative charges on chalcogen atoms attached to adjacent carbon atoms. Similarly for the monoalkylated derivative, the two canonical structures which are shown have the negative charge on the carbon adjacent



to the alkylated position. The observation of one singlet in the nmr spectrum suggests only one kind of chalcogen atom is being alkylated, and the shift value $\delta = 3.07$ ppm suggests S- rather than O-alkylation.[10] The dithiocroconate synthesized is therefore assigned a 1,2-dithiolene structure **1a**.

Electronic Spectra

The visible-uv spectra of K_2dtcroc in aqueous solution at several different acidities is shown in Figure I. Identical spectra were obtained in 10^{-4} M $HClO_4$ solution, pure water, and pH 9.2 buffer solution—therefore this spectrum is assigned to the dianionic form of dithiocroconate. The bands exhibit large values for molar absorptivity (>10^4), and must be considered as due to allowed transitions. The major spectral features of this and related compounds are reproduced in Table I. There is a marked similarity in the first absorption band of the dianions with regard to shape and intensity, and the shoulder is set off from the main peak by ~2.0×10^3 cm^{-1} in all cases. The wavelength increases upon substitution of sulfur atoms for two oxygen atoms in the oxocarbon ring, as well as with increasing size of the ring. Several factors can be considered when examining the first phenomenon.

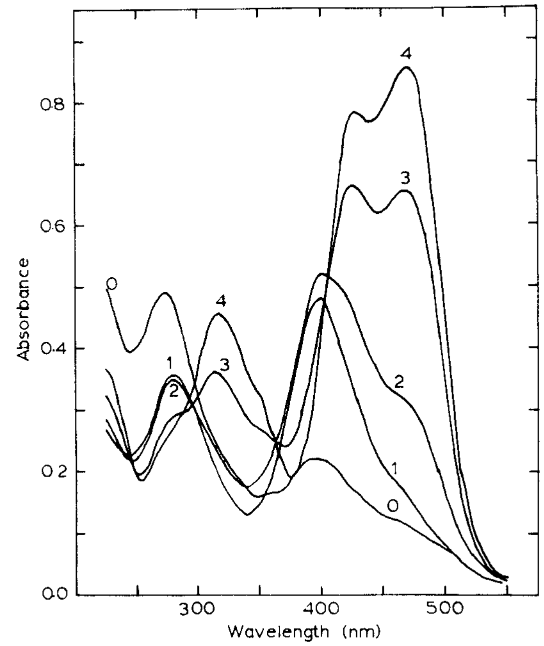


FIGURE I

Visible-uv spectra of 4.0×10^{-5} M $K_2C_5O_3S_2$ in aqueous solution at different acidities, pH 0 to pH = 4

TABLE I

Major Bands in Visible-uv Spectra of Oxocarbons and Derivatives

Substance	λ_{max}, nm
squarate, $C_4O_4{}^{2-}$	269[a]
dithiosquarate, $C_4O_2S_2{}^{2-}$	346, 325(sh)[b]
	250, 230
croconate, $C_5O_5{}^{2-}$	364, 340(sh)[c]
dithiocroconate, $C_5O_3S_2{}^{2-}$	471, 425(sh)[d]
	319
S,S'-dimethyldithiocroconate, $C_5O_3(SCH_3)_2$	371, 280[d]
rhodizonate, $C_6O_6{}^{2-}$	483[a]

[a]data from ref 4. [b]data from ref 2. [c]data from ref 12. [d]this work.

The lowest unoccupied π-electron level in $C_4O_4{}^{2-}$ and $C_5O_5{}^{2-}$ species[13] is doubly degenerate but these degeneracies are removed by descent in symmetry in $C_4O_2S_2{}^{2-}$ and $C_5O_3S_2{}^{2-}$. One also notes that $n_S \rightarrow \pi^*$ excitation would be expected to occur at lower energy than the corresponding $n_O \rightarrow \pi^*$ in the parent oxocarbon dianions.

The variation in the visible-uv spectra of $C_5O_3S_2{}^{2-}$ at higher acidities parallels the behavior of $C_5O_5{}^{2-}$ under similar conditions. For the latter, equilibria involved in these variations have been extensively studied and the pK's associated with the stepwise processes documented.[12,14]

$$\text{croc}^{2-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \text{Hcroc}^- \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2\text{croc} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_3\text{croc}^+$$

The croconate spectrum is unchanged down to $pH \simeq 2.7$ (10^{-3} M H_2SO_4), while the dithiocroconate spectrum exhibits recognizable alteration as the pH is lowered from 4 to 3, with the trend continuing as the pH is decreased further. We conclude that dithiocroconate is a stronger proton acceptor than croconate, and suggest that resonance stabilization in the croconate dianion must be substantially greater than in dithiocroconate since simple thiols are more acidic than their oxygen counterparts in the absence of resonance effects.

The electronic spectrum of the thioether, S,S'-dimethyldithiocroconate, with maxima at 371 nm and 280 nm, most closely resembles that of potassium dithiocroconate measured at pH = 1, which has maxima at 400 nm and 280 nm. It has already been noted that dithiocroconate dianion is a stronger Bronsted base than croconate, and this spectral evidence suggests that the second stepwise protonation may occur more readily in dtcroc^{2-} also. The general shape of the spectrum thus assigned to H_2dtcroc is similar to that reported by Carpentier for H_2croc—again it is noticed that maxima in the first-named species occur at longer wavelengths than the corresponding feature in the latter, which have maxima at 297 nm and 230 nm.[12]

Infrared Spectra

The infrared spectra of $K_2C_5O_3S_2$ and $C_5O_3(SCH_3)_2$ are reproduced in Figure II. The number of ir-active fundamentals predicted for a planar dianion of **1** with C_{2v} symmetry is 15, in contrast to the 4 expected and observed for planar $C_5O_5{}^{2-}$. Three fundamentals are associated with in plane C–O stretching vibrations, while two are associated with C–S stretching. In the planar $C_5O_5{}^{2-}$, three absorption maxima observed at 1718 cm^{-1} (vw), 1591 cm^{-1} (s), and 1570 cm^{-1} (vs, very broad) were assigned to two Raman-active and one ir-active C–O stretching modes respectively, by Ito and West.[15] In $C_5O_3S_2{}^{2-}$ maxima are observed in the ir at 1658 cm^{-1} (s), 1602 cm^{-1} (m), and 1564 cm^{-1} (vs, broad) while in $C_5O_3(SCH_3)_2$ maxima are observed at 1752 cm^{-1} (s), 1714 cm^{-1} (s), and 1673 cm^{-1} (vs). These maxima are also suggested as being associated with the in-plane C–O stretching modes, and the progressive shift to higher energies in the series $C_5O_5{}^{2-}$, $C_5O_3S_2{}^{2-}$, $C_5O_3(SCH_3)_2$ is indicative of the increasing order of the C–O bond. $C_5O_5{}^{2-}$ is a planar delocalized system with a calculated C–O bond order of 1.6.[13] $C_5O_3S_2{}^{2-}$ exhibits less delocalization of the negative charge to the oxygen atoms, hence the resulting C–O bond order should be >1.6 while the C–S value should be substantially less than 1.6. In terms of a localized bond model, the contribution to the resonance hybrid decreases as one progresses from structure **1a** through **1b**, **1e** to **1c**, **1d**.

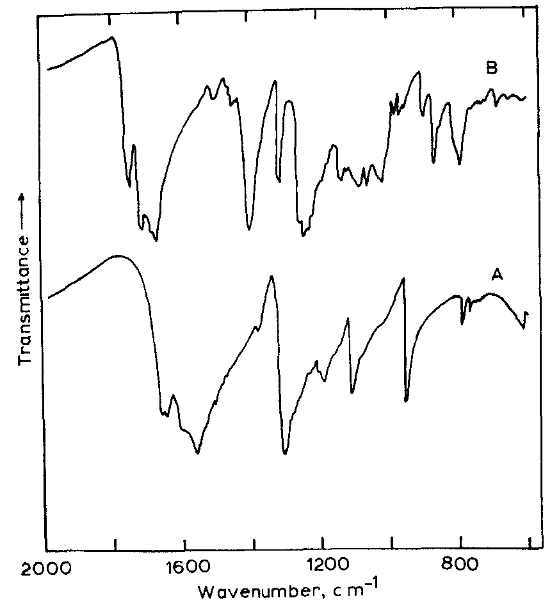
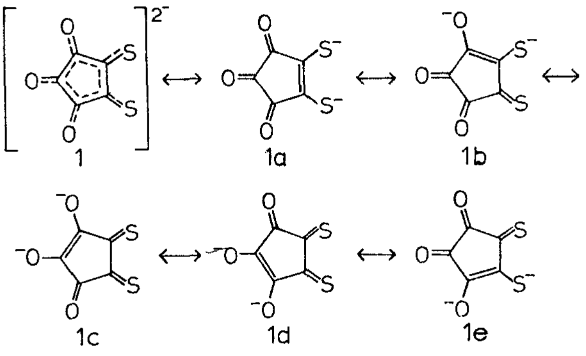


FIGURE II

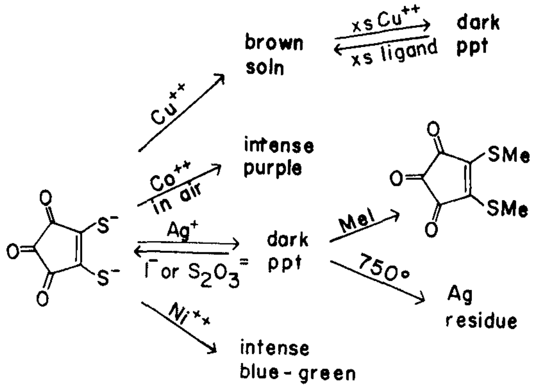
Infrared spectra in KBr of: (A) $K_2C_5O_3S_2$ (B) $C_5O_3(SCH_3)_2$



Finally, in $C_5O_3(SCH_3)_2$ no delocalization is expected and the bond order for the C–O should be 2.

Chemical Behavior

Some of the chemical reactions of dithiocroconate dianion are summarized in Scheme II. The alkaline earth salts are considerably more soluble than the related croconate salts, with the barium salt the least soluble. The ion forms highly colored species with transition metal ions in solution, and may be suitable as a colorimetric reagent. Some colors are: Cu(II), reddish brown. Ni(II), blue-green. Co(II), purple. Pd(II), magenta. Pt(II), royal blue. The silver salt, which is quantitatively precipitated from aqueous solution, dissolves in KI and $Na_2S_2O_3$ solutions to regenerate the free dithiocroconate dianion.



SCHEME II

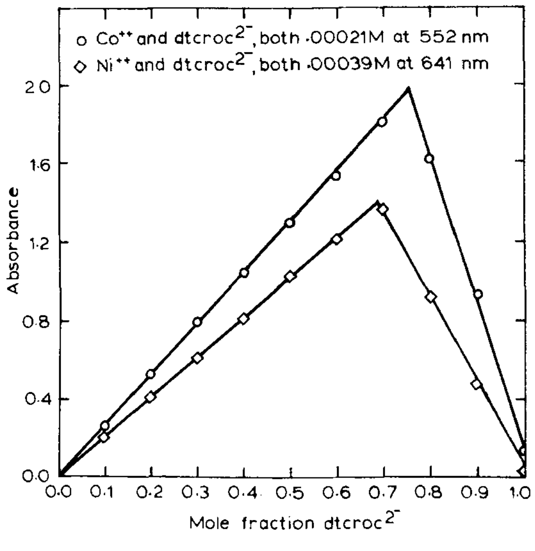


FIGURE III

Continuous variations plot for Co^{++} and Ni^{++} with $C_5O_3S_2^{2-}$

The reaction of Ni(II) and Co(II) in aqueous solution was followed spectrophotometrically using the method of continuous variations.[16] The results, shown in Figure III, indicate a 2:1 complex is formed with Ni(II) which is identical to the behavior observed with some other unsaturated 1,2-dithiolato ligands.[16,17] A 3:1 complex appears to be formed with Co(II) under similar conditions, but this reaction observed may involve aerial oxidation of the Co(II) complex to Co(III) and Co(III) often forms 6-coordinate *tris*-dithiolene complexes.

In a related study, dithiocroconate and Cu(II) were mixed in aqueous solution in 1:1 and 2:1 mole ratios, and the esr of both mixtures studied. At the 1:1 mole ratio an insoluble product separated, and the remaining solution gave a very weak resonance signal that was not investigated further. The esr of the reddish-brown solution containing the 2:1 L/M ratio is shown in Figure IV. The ⟨g⟩, ⟨a⟩, and progressively smaller linewidth of the hyperfine lines, as well as the splitting in the high field hyperfine line are all characteristic of planar 2:1 Cu(II) complexes with unsaturated dithiolato ligands.[1,18] These studies suggest the 1,2-dithiocroconate is functioning as a bidentate ligand, with 4-coordination preferred for Ni(II) and Cu(II). Further synthetic studies in these substituted croconate and rhodizonate systems, as well as synthesis and characterization of some of their complexes are in progress and will be reported subsequently.[19]

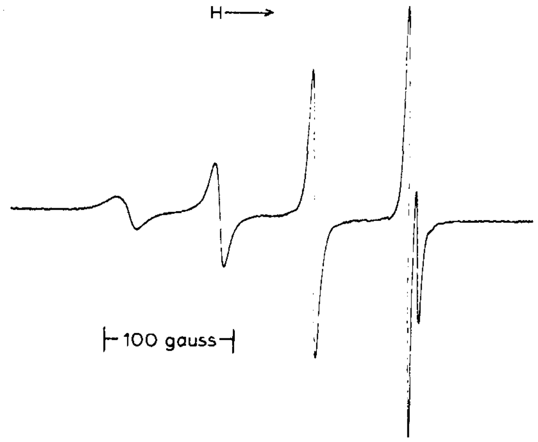


FIGURE IV

Esr spectrum of 2.8 x 10^{-3} M $Cu(C_5O_3S_2)_2^{2-}$ in aqueous solution

Acknowledgment

Financial support of this work by Xerox Corporation is gratefully acknowledged.

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