

chloride with 1,5-cyclooctadiene, the structure of which, in the solid state, has been reported recently.¹

It was found that at 2537 Å.² in ether solution (undegassed) (i) 1,5-cyclooctadiene (*c* 1%) by itself underwent hardly any photoreaction, although it has a weak absorption ($\epsilon \sim 10$) at this wave length³; (ii) 1,5-cyclooctadiene together with benzene (*c* 1%) as a sensitizer gave mainly a yellow polymer⁴; and (iii) the cuprous chloride-cyclooctadiene complex, which is sparingly soluble (solubility: 0.06 g./l. at 25°), gave rise to four products, all of which are believed to originate from the solvent *via* radical processes.

However, if about 1% of 1,5-cyclooctadiene was added to the solution of the complex as in (iii), it was observed that the quantum yield of the formation of the adducts was greatly diminished, while the chief product was tricyclo[3.3.0.0^{2,6}]octane (I). The latter was found to be identical in its infrared spectrum, refractive



I

index, and retention time on a gas chromatographic column with the material which had previously been synthesized in less than 1% yield by the mercury-photosensitized isomerization of 1,5-cyclooctadiene in the vapor phase.⁵ The yield of I in the present instance was 30%, which makes this a very convenient route to the synthesis of I in quantity.⁶

Although at first sight it appears that the π -complex sensitizes the photoisomerization of 1,5-cyclooctadiene by a transfer of electronic excitation energy, the reaction cannot be simply that. Ultraviolet absorption spectra of solutions of 1,5-cyclooctadiene (1%) and the π -complex (saturated) showed that the two solutions absorbed light at 2537 Å. to an equal extent. Further, the spectrum of the complex in solution was quite similar to that of cuprous chloride itself in ether solution (saturated). It would appear that in a saturated solution of the π -complex in ether, to which an excess of 1,5-cyclooctadiene had been added, the radiation is as likely to be absorbed by the π -complex as by free 1,5-cyclooctadiene.

Addition of 1,5-hexadiene instead of 1,5-cyclooctadiene to a solution of the π -complex in ether, followed by photolysis, did not lead to any isomerization of 1,5-hexadiene. The catalytic effect of the π -complex seems to be quite specific, which suggests that it may involve the formation in solution of a second complex between the original π -complex and the excess of cyclooctadiene. The details of the reaction mechanism are presently under investigation. Since numerous π -complexes of olefins with a great variety of inorganic compounds have been described,⁷ the present

method may lead to other interesting reactions of great utility in organic synthesis. For example, photolysis of 1,3-butadiene as a solution (1%) in ether in the presence of cuprous chloride is found to give a 30% yield of cyclobutene. Although photolysis of 1,3-butadiene by itself in solution does lead to cyclobutene, the addition of cuprous chloride makes it possible to carry out the reaction with 2537-Å. radiation and seems to involve fewer side reactions. However, it is not obvious if a complex between 1,3-butadiene and cuprous chloride is involved in this reaction. A complex that is structurally similar to the 1,5-cyclooctadiene complex is not possible with 1,3-butadiene.

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Concerning the Existence of High-Spin
Planar Cobaltous Complexes:
Bis(1,2-dicyanomaleonitriledithiolato)cobalt(II)
Dianion

Sir:

Several years ago it was shown from simple ligand field theory for d^7 systems that the spin multiplicity of the ground state of coordinated Co(II) could be either doublet or quartet in planar symmetry, depending upon the strength of the in-plane ligand field.¹ Consideration of the electronic properties of a series of high-spin cobaltous complexes of the type Co-O₄ led to exclusion of a tetrahedral structure. A planar configuration was suggested for these complexes, although stabilization of the quartet spin state due to axial perturbation of the in-plane field could not be excluded.² Hence, the existence of high-spin planar Co(II) complexes has been open to genuine question. There seems little doubt that four-coordinate low-spin complexes are planar.⁴

The most encouraging evidence to date for the existence of high-spin planar Co(II) complexes has been presented by Gray, *et al.*,⁵ who first prepared bis(1,2-dicyanomaleonitriledithiolato)cobalt(II) dianion, [CoS₄C₄(CN)₄]⁻² (1) and reported $\mu_{\text{eff}} = 3.92$ B.M. Our previous work^{6,7} demonstrates that this complex is one of a number of apparently planar species of the general type [MS₄C₄R₄]^z ($z = 0, -1, \text{ and } -2$) which are related by electron-transfer reactions and as such it is formally isoelectronic with [MS₄C₄R₄]⁻¹, M = Ni, Pd, and Pt; R = CN; M = Ni and Pt; R = CF₃; M = Ni; R = C₆H₅.^{6,7} In contrast to the reported behavior of 1, all of these complexes are low spin in the solid and in solution; in acetone all moments fall in the range 1.78–1.88 B.M. The comparison of 1 with the mononegative anions is especially pertinent. From a thorough magnetic susceptibility and electron spin resonance study of 1, we have concluded that this complex is, in fact, low-spin ($S = 1/2$).

(1) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(2) Evidence is accumulating that at least in one such complex, *viz.*, bis-(acetylacetonato)cobalt(II), molecular association in solution³ and an attendant increase in the effective coordination number above four may be partially responsible for the large magnetic moments (~ 4.8 B.M.) observed in solution.³

(3) D. P. Graddon, *Nature*, **195**, 891 (1962); J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963); F. A. Cotton and R. H. Soderberg, to be published.

(4) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954); *ibid.*, 338 (1959); R. Havemann, W. Haberditzl, and K.-H. Mader, *Z. Physik. Chem. (Leipzig)*, **218**, 71 (1961).

(5) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 2029 (1963).

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, in press.

(1) J. H. Van den Hende and W. C. Baird, Jr., *J. Am. Chem. Soc.*, **85**, 1009 (1963).

(2) The light source that was used has been described before [R. Srinivasan, *ibid.*, **83**, 4923 (1961)]. This source is now available from the Southern N. E. Ultraviolet Co., Middletown, Conn.

(3) Cyclohexene also has a weak absorption which extends to 2800 Å. Landolt-Bornstein, "Zahlenwerte und Funktionen," Vol. 1, Springer-Verlag, Berlin, 1951, part III, p. 262.

(4) Photosensitization of 1,5-cyclooctadiene by benzophenone leads mainly to polymer formation. (D. I. Schuster, private communication).

(5) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

(6) The preparation of I may be carried out by photolyzing for 40 hr. a saturated solution (2000 ml.) of the complex in ether to which 1,5-cyclooctadiene (12 ml.) had been added. It was desirable to filter and resaturate the solution after the first 20 hr. of irradiation. From the photolysate, the ether was removed by distillation following which fractionation gave I (5–6 ml.) and unreacted 1,5-cyclooctadiene (2 ml.). I was obtained pure by preparative gas chromatography.

(7) R. G. Guy and B. L. Shaw, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 4, edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1962, Chapter II.

Three salts of I have been prepared; their compositions are established by the data below.⁸ The good agreement among the magnetic moments (*cf.* Table I) of the pure crystalline solids and among the results for the $(n\text{-Bu}_4\text{N})^+$ salt in the pure solid, in solution, and in mixed crystals of the isomorphous diamagnetic $[(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]]$ leaves no doubt as to the authenticity of the doublet ground state and the lack of strong magnetic interactions in the pure solid. The lower Curie magnetic moments at 77°K. are often found for low-spin planar Co(II).^{4,9}

TABLE I
MAGNETIC MEASUREMENTS ON $[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$

Compound	State	μ_{eff} , B.M. ^a
$[(\text{C}_6\text{H}_5)_4\text{As}]_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.16
$(\text{Et}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.08
	Solid (77°K.)	1.87
$(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$	Solid	2.16
	Solid (77°K.)	1.93
	50.9% in Ni diluent	2.19
	32.9% in Ni diluent	2.18
	18.0% in Ni diluent	2.20
	11.5% in Ni diluent	2.22
	5.3% in Ni diluent	2.11
	Acetone soln.	2.17
	DMSO soln.	2.14
	DMF soln.	2.09

^a All measurements at 300°K. unless otherwise stated; all moments are calculated from the Curie law.

We have made extensive magnetic resonance measurements on I, the results of which appear in Table II. The single crystal measurements were made by rotating the magnetic field in three mutually perpendicular crystal planes, and the data were treated by least squares and analyzed according to the procedure outlined by Schonland.¹⁰

TABLE II
PARAMAGNETIC RESONANCE MEASUREMENTS ON
 $(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]^{-2}$

State	g -Values	Co ⁵⁹ hyperfine interaction (cm. ⁻¹)
Solution, acetone	2.255 ^b	...
20% solid solution in Ni diluent, powdered sample	$g_1 \sim g_2 \sim 2.0$ $g_3 = 2.80 \pm .01$	$ a_3 = 4.8 \times 10^{-3}$
5% solid solution in Ni diluent, single crystal	$g_1 = 1.977^c$ $g_2 = 2.025^c$ $g_3 = 2.798^c$	$ a_1 = 2.3 \times 10^{-3d}$ $ a_2 = 2.8 \times 10^{-3d}$ $ a_3 = 5.0 \times 10^{-3d}$

^a Measurements made at room temperature, ~298°K. ^b Single broad line, ~220 gauss peak-peak. g -Value reported is $(g)_{\text{av}}$, estimated accuracy ± 0.010 . ^c Estimated accuracy ± 0.003 . ^d Estimated accuracy $\pm 0.1 \times 10^{-3}$ cm.⁻¹.

The r.m.s. g -value of 2.297 obtained from the single crystal measurement requires for $S = 3/2$ a moment of 4.45 B.M. and for $S = 1/2$, 1.99 B.M. The reported high-spin moment is in poor agreement with the e.s.r. result, contrary to a previous conclusion based on the average of g_1 and g_2 only.⁵ Deviations of 0.1–0.2 B.M. between the Curie law moments (Table I) and the crystal g -values (Table II) may be due to thermal accessibility of excited electronic states.

(8) For $\text{R}_2\text{CoS}_4\text{C}_4(\text{CN})_4$ melting points, analyses, and conductivities (nitromethane) are as follows. *Anal.* R = $(n\text{-Bu}_4\text{N})$ (141–143°); Calcd: C, 58.29; H, 8.81; N, 10.25; S, 15.56. Found: C, 58.20; H, 8.78; N, 10.34; S, 15.80; $\Lambda = 161$. R = (Et_4N) (197.5–200°); Calcd: C, 48.06; H, 6.72. Found: C, 47.87; H, 6.51; $\Lambda = 181$. R = $(\text{C}_6\text{H}_5)_4\text{As}$ (227–230°); Calcd: C, 60.82; H, 3.65; N, 5.07. Found: C, 60.75; H, 3.70; N, 4.98; $\Lambda = 197$ cm.² equiv.⁻¹ ohm.⁻¹.

(9) We thank Professor F. A. Cotton for the use of low temperature magnetic susceptibility equipment.

(10) D. S. Schonland, *Proc. Phys. Soc. (London)*, **73**, 788 (1959).

It would be premature, without structural information, to identify the magnetic axis system in terms of the principal symmetry axes of the presumably planar ion 1. Especially dangerous would be the identification of g_3 with g_{\parallel} for the planar complex, in light of the paramagnetic resonance results on cobalt(II) phthalocyanine,¹¹ for which $g_{\parallel} = 1.92$, $g_{\perp} = 2.90$. It would perhaps be more reasonable to associate g_1 and g_2 in which case the large in-plane anisotropy must be explained by a significant splitting of the energies of the d_{xz} and d_{yz} orbitals by the ligand field. Such a splitting could arise if there is delocalization of these orbitals over the π -system of the ligands and would indeed be a consequence of the D_{2h} symmetry of the complex as contrasted with the D_{4h} symmetry of the phthalocyanine. However, the ground state configuration may not be the same in this complex as that deduced by Griffith¹² for cobalt(II) phthalocyanine.

Following are the d -spacings of all lines in the X-ray powder pattern of $(n\text{-Bu}_4\text{N})_2[\text{CoS}_4\text{C}_4(\text{CN})_4]$ occurring in the range $4 < d < 5$ Å.: 4.00(s), 4.12(w), 4.18(m), 4.50(m), 4.63(vw), 4.76(w), 4.88(s), 4.96(w), and 5.08(s).

Acknowledgment.—Financial support by the National Institutes of Health, National Science Foundation, and the Advanced Research Projects Agency (Contract SD-88) is gratefully acknowledged.

(11) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

(12) J. S. Griffith, *ibid.*, **26**, 81 (1958).

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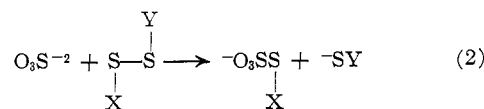
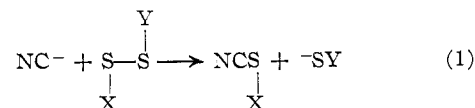
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A Novel Correlation of Activation Energy with Sulfur–Sulfur Bond Distance¹

Sir:

The sulfur–sulfur bond is unique in that the bond distance varies from 1.89 Å. in diatomic sulfur² to 2.39 Å. in sodium dithionite.³ While both of these extreme values are for atypical sulfur–sulfur bonds, numerous compounds contain sulfur–sulfur bonds from 1.97 to 2.2 Å. in length.^{4,5} In continuing an exploration of the SN2 reaction we expected to find some correlation between the length of the sulfur–sulfur bond and the activation energy of cleavage of that bond with various thiophilic reagents.⁶

Both cyanide ion and sulfite ion are good thiophilic reagents. In Table I the results of numerous investi-



gators on sulfur–sulfur bond lengths and activation energies of displacement reactions in aqueous media near 25° are presented. It is of interest to note (1)

(1) Displacement Reactions. IV. Paper III: R. E. Davis, *J. Phys. Chem.*, **66**, 956 (1962). Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) K. Ikenoue, *J. Phys. Soc. Japan*, **8**, 646 (1953).

(3) J. D. Dunitz, *Acta Cryst.*, **9**, 579 (1956).

(4) S. C. Abrahams, *Quart. Rev. (London)*, **10**, 407 (1956).

(5) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 16–24.

(6) R. E. Davis, Thesis, Harvard University, under P. D. Bartlett, 1958.