tances are longer than those of other dithiolate complexes, being 3.17 ± 0.01 (on twofold) and 3.11 ± 0.01 A for the other two ligands. Anaiogous distances have been found to be in the range 3.04–3.10 A in all other structures.[10]

A useful criterion for discussion of coordination geometry in the systems under consideration is the average S–M–S angle involving pairs of donor atoms that are farthest apart. This angle averages 136 ± 1° in the known trigonal-prismatic structures[2–6] and 180° for the perfect octahedron. However, we must first take into account the constraint imposed upon the idealized octahedron by the rigid nature of the maleonitriledithiolate ligands. Because of this constraint, the average for this angle in the chelated complex derived from an octahedron should be approximately 173°.[11] The average angle found for $V(mnt)_3^{2-}$ is 158.6°, which is somewhat closer to the "chelated octahedral structure." The observed distortion is not simply a solid-state phenomenon since the rich electronic spectrum of $V(mnt)_3^{2-}$ remains essentially identical for various cations (Me_4N^+, Et_4N^+, Bu_4N^+, and Ph_4As^+) in solid samples and in solutions. Furthermore, the infrared absorptions attributable to the anion are independent of the nature of the cation in solid samples. The distortion must then have an intramolecular electronic origin. We suggest that the two relatively short interligand S–S distances indicate some residual S–S bonding of the type which has been postulated as stabilizing the trigonal-prismatic structure in the uncharged complexes.[2] It is reasonable to expect the additional two electrons in the dianionic complex to cause the ligands to behave more like conventional dithiolates where a "classical" octahedral structure may be favored. Pitting these two effects against the geometric constants of the ligand, we can only say that nature has chosen an interesting compromise configuration; we have much work to do before we can begin to understand its subtleties.[12]

We have recently prepared the Ph_4As^+ salts of $M(mnt)_3^{2-}$ [13] for M = Ti, V,[8] Cr,[8] Mn,[14] Fe,[14] Mo,[14] W,[14] and Re. We find that the Ti, V, and Cr complexes have nearly identical X-ray powder patterns and thus appear isomorphous. It is also interesting to note the magnetic properties of these first-row complexes. If the ligands are considered to be dianions, then the central metal is in the formal IV oxidation state and the moments are found to be those typical of low-spin octahedral compounds (see Table II). Furthermore, spectral studies indicate a certain similarity in the electronic structures of the complex anions. In view of the evidence, then, we suggest that all the first-row $M(mnt)_3^{2-}$ complexes have distorted octahedral structures. Thus, the picture seems to be emerging that the more highly reduced species will approach the classical octahedral stereochemistry, while the oxidized forms will invariably possess the unusual trigonal-prismatic coordination.

Table II. Magnetic Properties of $M(mnt)_3^{n-}$ Complexes

Complex[a]	μ_{eff}, BM	Complex[a]	μ_{eff}, BM
$Ti(mnt)_3^{2-}$	Diamag[b]	$Fe(mnt)_3^{2-}$	3.00[b]
$V(mnt)_3^{2-}$	1.82[c]	$Cr(mnt)_3^{3-}$	3.90[c]
$Cr(mnt)_3^{2-}$	2.89[c]	$Co(mnt)_3^{3-}$	Diamag[b]
$Mn(mnt)_3^{2-}$	3.85[b]		

[a] Cation is Ph_4As^+. Magnetic moments are for solid samples at room temperature. [b] Details reported in ref 13. [c] From ref 8.

---

(10) (a) This is true for the three prismatic structures,[2–6] the six square-planar structures,[10b–g] and the two dimeric structures[10h,i] which have been fully solved; (b) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 605 (1965). (c) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, 3, 1501 (1964); (d) *ibid.*, 3, 1507 (1964); (e) C. J. Fritchie, Jr., *Acta Cryst.*, 20, 107 (1966); (f) D. Sartain and M. R. Truter, *Chem. Commun.*, **382**, (1966); (g) R. Eisenberg, Z. Dori, J. A. Ibers, and H. B. Gray, to be published; (h) J. M. Enemark and W. N. Lipscomb, *Inorg. Chem.*, 4, 1729 (1965); (i) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, to be published.

(11) For comparison, in $Cr(C_2O_4)_3^{3-}$, where the average "bite" O–Cr–O angle is 82°, we have calculated the average (largest) O–Cr–O angle to be 172° [J. N. van Niekerk and F. R. L. Schoenig, *Acta Cryst.*, **5**, 499 (1952)].

(12) For example, the V atom lies significantly out of the planes determined by the ligands alone. Pertinent geometrical parameters (such as interligand dihedral angles) determined solely from the MS_6 framework tend toward octahedral structure whereas related parameters set by the ligand planes suggest structure closer to trigonal prismatic. This finding may indicate that the ligand unit "prefers" the prism structure whereas the metal is desirous of octahedral coordination. Another interesting result arises on comparison of the C–C bond lengths in this structure with corresponding parameters from the $V(S_2C_2Ph_2)_3$ structure.[3,6] The pertinent distances for $V(mnt)_3^{2-}$ are 1.37 ± 0.02 (two distances related by twofold axis) and 1.29 ± 0.03 A, whereas the corresponding distances for $V(S_2C_2Ph_2)_3$ are 1.38 ± 0.01 and 1.46 ± 0.02 A. The drastic shortening of one C–C bond (from 1.46 to 1.29 A) suggests that the ligands do not participate equally in the two-electron reduction described by $VL_3 + 2e \rightarrow VL_3^{2-}$.

(13) E. I. Stiefel, L. Bennett, Z. Dori, C. Simo, T. H. Crawford, and H. B. Gray, to be published.

(14) Salts of these anions have also been prepared by M. Gerlock, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.*, 29 (1966). The magnetic results reported initially by these authors for the Mn and Fe compounds are apparently in error; our results are in agreement with their latest values (J. A. McCleverty, private communication).

(15) National Science Foundation Graduate Fellow, 1965–1967.

Edward I. Stiefel,[15] **Zvi Dori**
Department of Chemistry, Columbia University
New York, New York 10027
Harry B. Gray
Contribution No. 3499
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California
Received March 9, 1967

Chronology in Photochemical Mechanisms. The Reaction of 6-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one. Mechanistic Organic Photochemistry. XXV[1]

Sir:

One of the most challenging questions in photochemistry concerns the chronology in photochemical reaction mechanisms. In particular, one would like to know at which point in a transformation electronic excitation is lost.

In the type B rearrangement[2] of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones the first step seems without doubt to be fission of bond 2–4 (cyclohexane numbering; see Chart I) of the triplet[3] excited state (**1***) of the bicyclic ketone; fission of this internal three-ring bond converts carbons 2 and 4 to valency-deficient centers to which aryl (or alkyl in nonaryl cases) migration might occur. However, the migration to C-2 and C-4 could occur immediately following bond 2–4 fission and therefore be a reaction of a triplet excited state (*e.g.*, **2***), or

---

(1) For paper XXIV see H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Am. Chem. Soc.*, in press.

(2) See H. E. Zimmerman, *Science*, **153**, 837 (1966).

(3) Evidence for involvement of the triplet has been presented by H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Am. Chem. Soc.*, **88**, 4895 (1966).

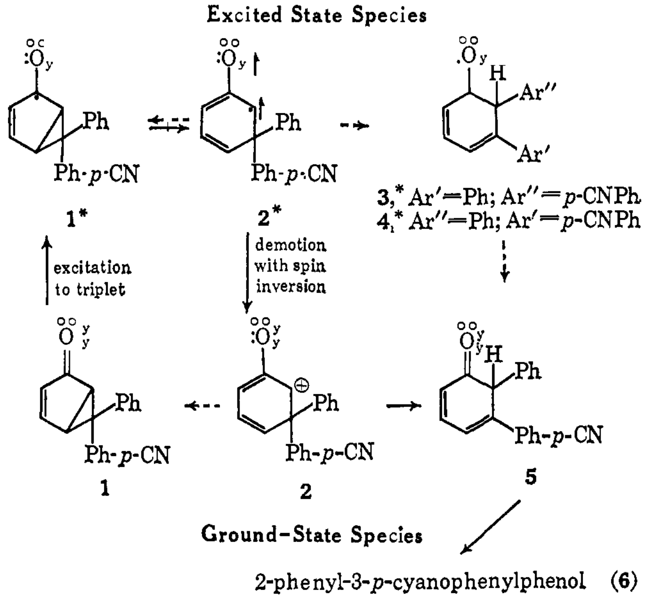
Table I. Irradiation Runs of 6-*p*-Cyanophenyl-6-phenyl[3.1.0]bicyclohex-3-en-2-one

				Product distribution, %[a,b]		
Run	Reactants	Type run	Recovered bicyclic[b,c] ketone, %	2-Phenyl-3-*p*-cyanophenyl-phenol	3-*p*-Cyanophenyl-4-phenyl-phenol	Photo acids[f]
1	Ketone **1a**	*d*	86	34 ± 1	12 ± 2	55 ± 4
2	Ketone **1a**	*d*	35	37 ± 1	12 ± 2	51 ± 4
3	Ketone **1b**	*d*	71	14 ± 1	6 ± 2	80 ± 5
4	Ketone **1b**	*d*	45	22 ± 1	7 ± 1	70 ± 4
5	Ketone **1a**	*e*	89	45 ± 2	23 ± 6	32 ± 4
6	Ketone **1b**	*e*	86	43 ± 2	21 ± 6	37 ± 4

[a] Per cent of products other than recovered bicyclic ketone. [b] Mass balance 100 ± 2%. [c] Per cent based on total material. [d] Direct irradiation runs. [e] Sensitized runs with acetophenone absorbing over 97% of the light. [f] 6,6-Diaryl-3,5-hexadienoic acid stereoisomers (see ref 3).

instead might follow electron demotion and thus be a reaction of the ground-state zwitterion **2**. The latter mechanism is the one proposed by us earlier[4] to account for the products of the type B process.

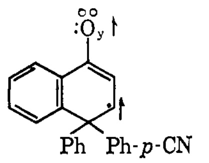
Chart I[a]



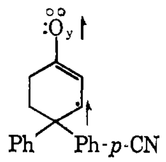
[a] Processes ruled out, — — —.

An approach likely to provide the answer involved the study of the photochemical behavior of 6-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (**1**). If the electronically excited state **2*** rearranges after 2,4-bond fission, then *p*-cyanophenyl migration should be preferred. Such a result would be in accord with Rüchardt's finding of a strong preference (19:1 to 35:1) for cyanophenyl over phenyl migration in free-radical rearrangements.[5] Additionally, such a result would have analogy in our earlier studies of excited-state migratory aptitudes; here the excited states of 4-phenyl-4-*p*-cyanophenyl-1(4H)-naphthalenone (**8**) and 4-phenyl-4-*p*-cyanophenylcyclohexenone (**9**) were shown to undergo a preferred *p*-cyanophenyl migration (2.2:1 for **8***; 15:1 for **9***) to the *β* carbon of the excited enone moiety.[6,7]

On the other hand, if the ground-state zwitterion rearranges, preferential phenyl migration should ensue since phenyl bearing an electron-withdrawing group as cyano should not migrate readily to a cationic center.



8*



9*

6-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (**1**) was prepared by a synthesis involving irradiation of 4-phenyl-4-*p*-cyanophenylcyclohexadienone (**10**) and affording both epimers of **1**.[8]

The results of irradiation of 6-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hex-3-en-2-one (**1**) are collected in Table I. The first striking observation noted is that irradiation of either stereoisomer of **1** gives the *same* distribution of phenolic products, with the 2,3-diarylphenol predominating over the 3,4 isomer, as was the case for the diphenyl analog. Additionally, it was found that on short irradiations recovery of bicyclic ketone gave only the stereoisomer used as reactant. Thus there is evidence for a species common to both reactant stereoisomers in which the internal three-ring bond is broken and memory of the reactant stereochemistry is lost. Furthermore, once this central bond is broken, there is no reclosure; such reclosure would afford a mixture of bicyclic ketones. Other three-ring bond openings followed by free rotation are similarly precluded.

Secondly, there is a dramatic contrast between the previously studied cases where cyanophenyl migrates in preference[6,7] and the present reaction where only phenyl migration is observed. Thus, mainly 2-phenyl-3-*p*-cyanophenylphenol (**6**) and smaller quantities of 3-*p*-cyanophenyl-4-phenylphenol (**7**) were found. No *p*-cyanophenyl migration products could be detected. The preferred phenyl migration provides strong support for zwitterion **2** being the species undergoing aryl migration, and electron demotion thus occurring prior to the migration. We note that it is insufficient to select one group as migrating preferentially in photochemical reactions; one must inspect the details of the reaction and determine at which stage migration occurs. In the present instance of the type B rearrangement the scheme

---

(4) (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 1196 (1961); (b) *ibid.*, **84**, 4527 (1962).

(5) C. Rüchardt and S. Eichler, *Ber.*, **95**, 1921 (1962); C. Rüchardt and R. Hecht, *ibid.*, **98**, 2471 (1965).

(6) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Am. Chem. Soc.*, **87**, 1138 (1965).

(7) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

(8) Synthetic details and structure proofs will be reported in our full paper in press. All new compounds were properly characterized and acceptable elemental analyses were obtained.

in Chart I rationalizes the information[9] that the triplet excited state[10] of product is not reached.

Acknowledgment. Support of this research by a National Science Foundation Predoctoral Fellowship for J. O. G. and by an Army Research Office (Durham) grant is gratefully acknowledged.

---

[9] The demotion is shown as occurring just subsequent to internal three-ring bond fission with **2*** pictured as a discrete species; this is a convenience. Thus **2*** may not be an energy minimum, and demotion may occur by crossing or close approach of potential energy surfaces[2] and change in configuration at a slightly earlier or later point in the transformation.

[10] The intervention of the triplet in the phenol-forming reactions is suggested by the formation of the same products in the photosensitized runs as in the direct runs and by analogy to the diphenyl analog[3] where the phenolic product was shown to arise from the triplet and the acidic product from triplet and singlet.

Howard E. Zimmerman, Joan O. Grunewald
Chemistry Department, University of Wisconsin
Madison Wisconsin

Received April 7, 1967

Molecular and Electronic Structure of Pentacyanocobaltate[1]

Sir:

The complex $Co(CN)_5^{3-}$ has occasioned a good deal of interest in late years. Its action as a hydrogenation catalyst[2] for certain unsaturated organic molecules and the kinetics of its free-radical type reactions with some organic halides[3,4] have been subjects of recent investigation. Esr and optical spectral studies[5,6] of oxidation products of $Co(CN)_5^{3-}$ have also been carried out.

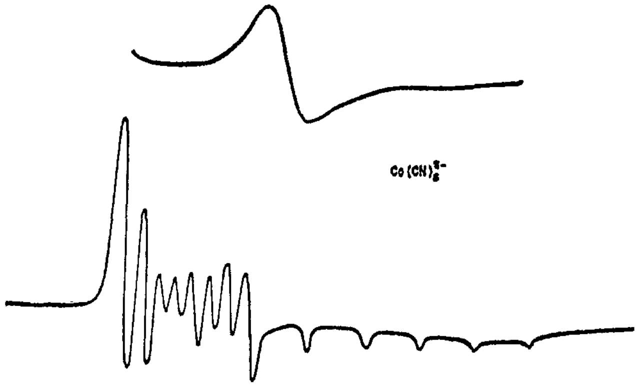


Figure 1. Electron spin resonance spectra for $Co(CN)_5^{3-}$ in 2:1 ethylene glycol–water: upper curve, 300°K; lower curve, 77°K in frozen solution. Spectra in pure ethylene glycol are not significantly different.

Up to now, the geometry of $Co(CN)_5^{3-}$ in solution has been unknown; supposing it to be five-coordinate, the two most likely idealized spatial arrangements are the trigonal bipyramid (of D_{3h} symmetry) and the square pyramid (of C_{4v} symmetry). (This latter symmetry would also hold if weak axial solvation made the complex six-coordinate.)

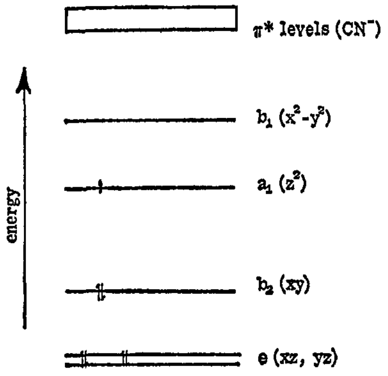


Figure 2. Partial diagram of electronic energy levels and suggested ground state for square-pyramidal $Co(CN)_5^{3-}$.

We have measured optical and esr spectra of pentacyanocobaltate(II) under a variety of conditions; here we show how the data from these experiments point to an idealized square-pyramidal ground-state geometry for this system.

Solutions for esr spectra were prepared by dissolving $K_6Co_2(CN)_{10}\cdot 4H_2O$[7] in 2:1 ethylene glycol–water and in pure ethylene glycol. Examination of the optical spectra of these solutions at 300°K and frozen at 77°K reveals the absorption pattern characteristic of the paramagnetic ($S = {}^1/_2$), monomeric $Co(CN)_5^{3-}$ species.[8] In particular, the intensity of the band peaking at 10,350 cm^{-1} shows $Co(CN)_5^{3-}$ to be the predominant species under the conditions of our experiment at 77°K. Confirmation of the existence of $Co(CN)_5^{3-}$ in the frozen solutions was necessary in light of results which indicate that dimerization and oxidation may readily occur under these conditions.[5,6]

Figure 1 shows esr spectra for $Co(CN)_5^{3-}$ at 300 and 77°K. At 300°K, a broad resonance lacking hyperfine structure and centered at $g = 2.11 \pm 0.01$ is seen. On freezing the solution at the lower temperature, the pattern observed is a 16-line resonance expected from an axially symmetric ^{59}Co ($I = {}^7/_2$) species, with two of the $g_{\|}$ lines hidden under the second and fifth lines of the $g_{\perp}$ pattern. Analysis of this spectrum gives $g_{\|} = 1.992 \pm 0.005$, $g_{\perp} = 2.157 \pm 0.005$, and hyperfine tensor components $A = 87 \pm 2$ and $B = 28 \pm 2$ gauss.

The axial symmetry of the g tensor combined with the value of 1.992 for $g_{\|}$ strongly suggest a square-pyramidal structure for $Co(CN)_5^{3-}$ with the unpaired electron placed in an orbital of d_{z^2} symmetry ($^2A_1$ ground state). This is nicely compatible with the electronic energy levels expected for a square-pyramidal pentacyano complex (Figure 2). The ground state in a d^7 case would be $(e)^4(b_2)^2(a_1)^1 = {}^2A_1$. Furthermore, none of the ground-state possibilities in a trigonal-bipyramidal geometry is consistent with the esr results.[9]

The electronic spectrum of $Co(CN)_5^{3-}$ in aqueous solution shows[8] bands at 10,350 cm^{-1} (ϵ 233), 16,200 (7), 23,300 (65), 31,700 (527), 35,700 (4030), 38,100 (980 sh), and 43,300 (6500). The rich pattern of weak-

---

[1] This research was supported by the National Science Foundation.

[2] J. Kwiatek, I. L. Mader, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemistry Society Washington, D. C., 1963, p 201.

[3] J. Halpern, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

[4] (a) J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965); (b) J. Halpern and P. J. Maher, **87**, 5361 (1965).

[5] J. H. Bayston, F. D. Looney, and M. E. Winfield, *Australian J. Chem.*, **16**, 557 (1963).

[6] J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *ibid.*, **16**, 954 (1963).

[7] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

[8] Our electronic spectral measurements are in essential agreement with those reported by N. K. King and M. E. Winfield, *ibid.*, **73**, 3366 (1951).

[9] The ground state $(e'')^4(e')^3 = {}^2E'$ expected for D_{3h} $Co(CN)_5^{3-}$ should give $g_{\|} \gg 2.0$. The fact that a slight Jahn-Teller distortion would be expected does not affect this conclusion.