PHYSICAL AND INORGANIC CHEMISTRY

Ligand Field Theory of Transition Metal Cyanide Complexes. Part I. The Zero, One and Two Electron or Hole Configurations[1]

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RECEIVED JUNE 2, 1962

The magnetic and spectroscopic demeanor of cyano-transition metal compounds is discussed from the standpoint of the modern theory of ligand fields. It is emphasized that for such compounds the naive electrostatic crystal field theory is inapplicable, and that the more general molecular orbital based crystal field theory (the so-called ligand field theory) is required to rationalize the existent experimental data. Equations which determine the spectral characteristics of zero, one, and two electron or hole cyanide compounds are derived, and their theoretical and experimental consequences are investigated. The prospects for future progress in this area are commented upon, and the avenues of greatest promise are mapped. Hope is expressed that such progress will soon circumscribe the domain of applicability of simple ligand field techniques.

Introduction

Of the various aspects of the chemistry and physics of Werner complexes which have been studied latterly, those which have been scrutinized most intensely, both qualitatively and quantitatively, have been their magnetochemical and spectrochemical behaviors.[3] And although great success has been met of late in understanding the magnetic and spectroscopic deportment of a large number of such complexes, the cyanides have as yet eluded all efforts to codify their optical transitions. For the most part this failure has arisen because of the inapplicability of the electrostatic crystal field theory to such systems.[3] But the failure has not been entirely complete. In 1935, Howard[4] explained the magnetic demeanor of the ferricyanide ion,[5] and others have since noted that the chromicyanide ion is also explicable on the basis of the simple theory of crystalline fields. Extensions of this simple technique to other cyanide complex ions have met with discouraging results. We shall show, however, that a slightly more sophisticated crystalline field treatment which uses a molecular orbital basis (the so-called ligand field method[3f]) can yield a satisfactory explanation of the magnetic and spectroscopic properties of the transition metal cyanides.[6-8]

Experimental

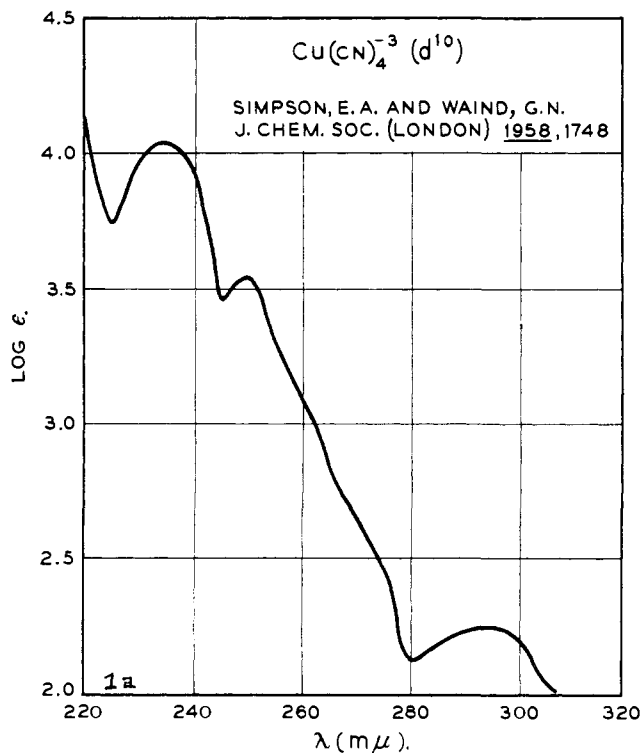**Preparations.**—Preparations were generally carried out as prescribed in references 10–15.

(1) This paper is based, in part, on a thesis submitted in June, 1962, by one of us (J. R. P.) to the Department of Chemistry, University of Southern California, in partial fulfillment of the requirements for the Ph.D. degree. A portion of this material was presented at the Symposia on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 1961 and 1962.

(2) (a) University of Southern California. (b) The Mellon Institute. (c) Bell Telephone Laboratories, Inc., and the Mellon Institute.

(3) (a) D. S. McClure, "Solid State Physics," Eds. F. Seitz and D. Turnbull, Academic Press, Inc., New York, N. Y., Vol. 9, 1959; (b) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961; (c) L. E. Orgel, "An Introduction to Transition-Element Chemistry. Ligand Field Theory," Methuen, London, 1960; (d) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, New York, N. Y., 1961; (e) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (f) A. D. Liehr, J. Chem. Educ., 39, 135 (1962); (g) C. K. Jørgensen, "Solid State Physics," Eds. F. Seitz and D. Turnbull, Academic Press, Vol. 13, 1962.

(4) J. B. Howard, J. Chem. Phys., 3, 813 (1935). Howard realized full well that he was actually using a simplified molecular orbital theory a la Van Vleck, rather than the elementary electrostatic crystal field theory.

(5) C. S. Naiman [ibid., 35, 323, 1503 (1961)] has recently examined the optical spectra of the ferricyanide and nitrosylchromocyanide anions from the theoretical standpoint; and H. B. Gray and C. J. Ballhausen [ibid., 36, 1151 (1962)] have done the same for the nitrosylchromo-, mangano- and ferrocyanide anions.

(6) M. B. Robin has independently utilized a similar treatment lately in his theoretical and experimental studies of the mixed valence transition metal dye materials such as prussian blue. See M. B. Robin, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, Columbus, Ohio, June, 1961; "Symposium on Ligand Field Theory," 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961; Inorg. Chem., 1, 337 (1962).

(7) F. J. Gilde and M. I. Ban have also used the molecular orbital method to treat (a) the hexacyanochromium(III) anion [F. J. Gilde and M. I. Ban, Acta Univ. Szegediensis Acta Phys. et Chem. [N.S.], 3, 42 (1957), (b) the tetracyanonickel(II) anion [M. I. Ban, Acta Chim. Acad. Sci. Hung., 19, 459 (1959)], and (c) the hexacyano-manganese(III), -iron(III) and -cobalt(III) anions [F. J. Gilde, Acta Univ. Szegediensis Acta Phys. et Chem. [N.S.], 6, 3 (1960)]. All these treatments follow the Wolfsberg–Helmholz scheme.[8] [Unfortunately, these treatments are marred by the neglect of a portion of the available bonding π-electron pool (cf. Fig. 2a, c, 4, 5 and 10a of the present paper).] A highly naive model of chemical ligature and spectra based upon simple overlap considerations has also been applied to the hexacyano-iron(II) and -cobalt(III) anions (amongst others) by (d) A. Bertoluzza and A. Marinangeli, Ann. Chim. (Rome), 49, 808 (1959), et seq.

(8) S. Kida, J. Fujita, K. Nakamoto and R. Tsuchida [Bull. Chem. Soc. (Japan), 31, 79 (1958)] have utilized the modified molecular orbital technique of M. Wolfsberg and L. Helmholz [J. Chem. Phys., 20, 837 (1952)] to compute the energy levels of copper(I) and nickel(II) tetracyanide and chromium(III) and cobalt(III) hexacyanide, amongst others, and have compared their results favorably with experiment. Where overlap exists, our ligand field results differ in several important respects from those of the Japanese authors. The interested reader is urged personally to compare the two alternative methods. It has been demonstrated elsewhere that spurious results are sometimes obtained from the Wolfsberg–Helmholz method.[9]

(9) Witness, for example, (a) C. J. Ballhausen and A. D. Liehr, J. Mol. Spectry., 2, 342 (1958) [Errata, ibid., 4, 190 (1960)]; (b) A. Carrington and C. K. Jorgensen, Mol. Phys., 4, 395 (1961); (c) M. C. R. Symons, "Advances in the Chemistry of the Coördination Compounds," Ed. S. Kirschner, The Macmillan Co., New York, N. Y., 1961.

(10) K₃W(CN)₈ and K₄W(CN)₈: E. L. Goodenow and C. S. Garner, J. Am. Chem. Soc., 77, 5268 (1955).

(11) K₃Mo(CN)₈: W. R. Bucknall and W. Wardlaw, J. Chem. Soc., 2986 (1927).

(12) K₄Mo(CN)₈: N. H. Furman and C. O. Miller, "Inorganic Synthesis," Ed. L. F. Audrieth, McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 3, 1950.

Figure 1a

$Cu(CN)_4^{-3}$ (d^{10})

SIMPSON, E. A. AND WAIND, G. N.
J. CHEM. SOC. (LONDON) 1958, 1748

λ_{MAX} (mμ)	ν_{MAX} (cm.$^{-1}$)	ϵ_{MAX}
235	42,550	$\sim$ 11,000
250	40,000	$\sim$ 3,540
265(S)	37,740	$\sim$ 660
295	33,900	$\sim$ 170

Figure 1a

Figure 1c

$Cu(CN)_2^{-}$ (d^{10})

SIMPSON, E. A. AND WAIND, G. N.
J. CHEM. SOC. (LONDON) 1748, (1958)
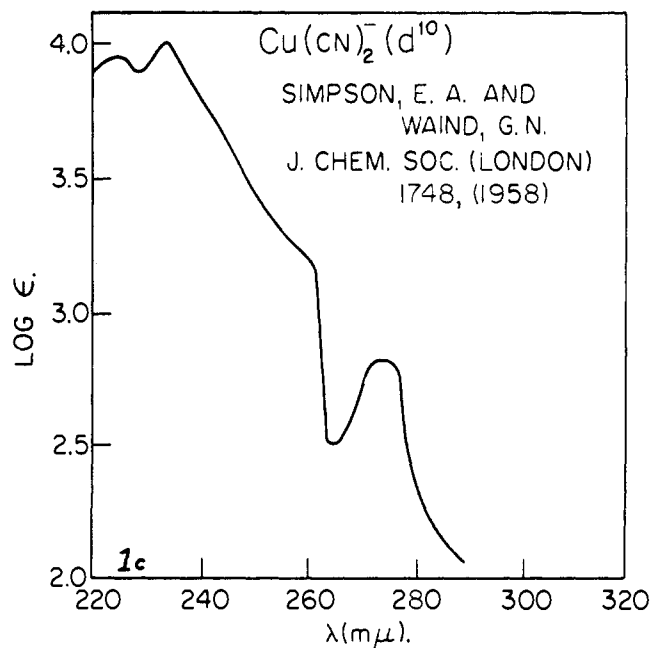
λ_{MAX} (mμ)	ν_{MAX} (cm.$^{-1}$)	ϵ_{MAX}
225	44,440	9,160
234	42,735	10,590
260(S)	38,460	1,637
274	36,496	650

Figure 1c

(1) $Zn(CN)_4^=$ (d^{10})
(2) $Cd(CN)_4^=$ "
(3) $Hg(CN)_4^=$ "
(4) $Ag(CN)_4^\equiv$ "

J. BRIGANDO,
BULL. CHIM. SOC. FRANCE
4, 503 (1957)

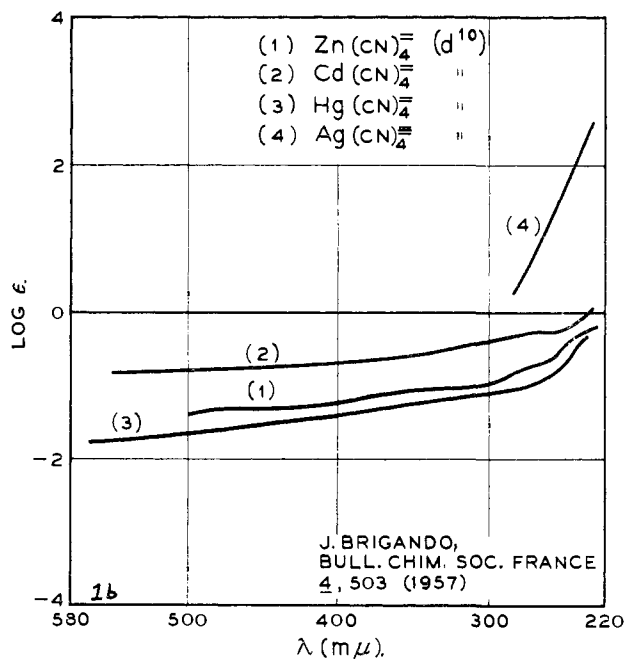Figure 1b

(1) $Ag(CN)_2^-$ (d^{10})
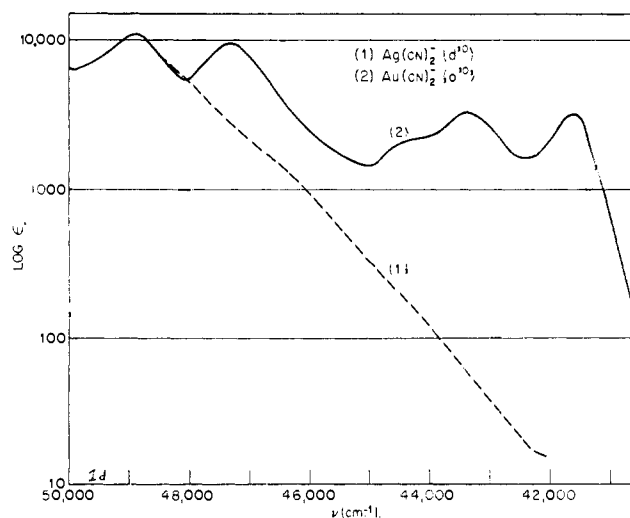(2) $Au(CN)_2^-$ (d^{10})

Figure 1d

Fig. 1a, b, c, d.—The absorption spectra of the d^{10} transition metal cyanide complex anions. Figures 1a, c show the spectra of the copper(I) complexes, and Figures 1b, d the spectra of the zinc(II), cadmium(II), mercury(II), silver(I) and gold(I) complexes.

(13) K₃Re(CN)₈ and [Co(NH₃)₆]₂[Re(CN)₈]₃: R. Colton, R. D. Peacock and G. Wilkinson, *J. Chem. Soc.*, 1374 (1960).

(14) Na₃V(CN)₆: A. G. MacDiarmid and N. F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).

(15) (a) K₂Ni(CN)₄: W. C. Fernelius and J. J. Burbage, "Inorganic Synthesis," Ed. W. C. Fernelius, McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 2 (1946); (b) KAu(CN)₄: A. Wogrinz, *Prakt. Chem.*, **3**, 5 (1952).

TABLE I

SPECTRAL DATA FOR THE d¹⁰ TRANSITION METAL CYANIDE COMPLEX ANIONS

	λ_{max}, mμ	ν_{max}, cm.⁻¹	ϵ_{max}	$f \times 10^{-4}$		Assignment
$Cu(CN)_4^{-3}$	234	42,740	11,000^{a,b}	Charge transfer		$^1A_1 \rightarrow\ ^1T_2$
	250	40,000	3,500^a	Charge transfer		$^1A_1 \rightarrow\ ^1T_2(?)$
	265(s)	37,740	600^a	Charge transfer	}	$^1A_1 \rightarrow\ ^1T_1,\ ^1E,$ or $^1A_1(?)$
	295	33,900	190^{a,b}	Charge transfer		
$Zn(CN)_4^=$	600–200	16,667–50,000	<1^c	Tail of charge transfer band		
$Cd(CN)_4^=$	600–200	16,667–50,000	<1^c	Tail of charge transfer band		
$Hg(CN)_4^=$	600–200	16,667–50,000	<1^c	Tail of charge transfer band		
$Ag(CN)_4^\equiv$	No absorptions in the visible region down to 263 mμ (38,462 cm.⁻¹)					
$Cu(CN)_2^-$	225	44,444	9,162^a	Charge transfer		$^1\Sigma_g^+ \rightarrow\ ^1\Sigma_u^+$
	234	42,735	10,590^a	Charge transfer		$^1\Sigma_g^+ \rightarrow\ ^1\Pi_u$
	260(s)	38,462	1,637^a	Charge transfer	}	$^1\Sigma_g^+ \rightarrow\ ^{1,3}\Sigma_g^+,\ ^{1,3}\Pi_g,\ ^3\Sigma_u^+$ or $^3\Pi_u(?)$
	274	36,496	650^a	Charge transfer		
$Ag(CN)_2^-$	Continuous absorption starting from 260 mμ (38,462 cm.⁻¹) toward the ultraviolet; absorption max. probably at wave lengths less than 230 mμ (>43,478 cm.⁻¹)^c					
$Au(CN)_2^-$	205	48,800	11,100^d	600		$^1\Sigma_g^+ \rightarrow\ ^1\Sigma_u^+$
	211.5	47,400	9,400^d	770		$^1\Sigma_g^+ \rightarrow\ ^1\Pi_u$
	230.3	43,400	3,450^d	280	}	$^1\Sigma_g^+ \rightarrow\ ^{1,3}\Sigma_g^+,\ ^{1,3}\Pi_g,\ ^3\Sigma_u^+,$ or $^3\Pi_u(?)$
	239.6	41,800	3,300^d	110		

^a Simpson and Waind.²⁰   ^b Kida, Fujita, Nakamoto and Tsuchida.⁸   ^c Brigando.¹⁹   ^d C. K. Jørgensen.⁴⁰

Absorption Spectra.—The spectra were measured in solution [with the exception of the [Co(NH₃)₆]₂[Re(CN)₈]₃ spectrum which was run in a KBr mull] on a Cary model 14 recording spectrophotometer in the region of 750–210 mμ and on a Beckman DU model in the region below 750 mμ.

Gaussian Analysis.—The absorption spectra were plotted on a frequency scale and resolved into Gaussian bands.¹⁶ The actual resolution was accomplished by fitting the most intense peaks (these were usually located in the ultraviolet region) to a Gaussian form first, and then subtracting this Gaussian form from the experimental curves. The process was then continued on the resultant difference curve. We have shown in the figures the *exact* fitting of the experimental curves rather than the sum of the derived Gaussian forms; hence, the asymmetrical appearance of some of the fitted forms.

Theory and Interpretation

The Zero Electron or Hole Configurations.—No transition metal cyanide complex compounds with d⁰-electronic configurations are known, and only eight well characterized (both chemically and physically) cyanide complexes with the d¹⁰-configuration are known: three of the type $M(CN)_4^{-2}$, M = Zn(II), Cd(II) and Hg(II); two of the type $M(CN)_4^{-3}$, M = Cu(I) and Ag(I); and three of the type $M(CN)_2^{-1}$, M = Cu(I), Ag(I) and Au(I). A tetrahedral geometry has been established for the complex anions in the first category,¹⁷ᵃ and a linear geometry for those in the third.¹⁷ᵇ,ᶜ,ᵈ,ᵉ We have assumed that the anions of the second category are structurally isomorphous to those of the first.¹⁷ᵉ,ᶠ,¹⁸ In Fig. 1a, b, c, d we show the spectra of these complexes according to Brigando,¹⁹ Simpson and Waind,²⁰ Kida, et al.,⁸ and ourselves and in Table I we summarize the observed spectral data. Schematic energy level diagrams for ligand fields of tetrahedral and axial symmetry are depicted in Fig. 2a, b, c.³ᶠ We have omitted from the energy level patterns of Fig. 2a, b, c the levels

(16) See, for example, C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

(17) (a) R. G. Dickenson, *J. Am. Chem. Soc.*, **44**, 774, 2404 (1922); (b) J. L. Hoard, *Z. Krist.*, **A84**, 231 (1933); (c) E. Staritzky and F. H. Ellinger, *Anal. Chem.*, **28**, 419, 420 (1956); (d) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957); (e) A. Rosenzweig and D. T. Cromer, *Acta Cryst.*, **12**, 709 (1959).

(18) There do exist considerable infrared and Raman data to support this assumption. Read (a) I. Damaschun, *Z. physik. Chem.*, **B16**, 81 (1932); (b) P. Chiorboli and C. Testa, *Ann. Chim. (Rome)*, **47**, 639 (1957); (c) G. B. Bonino and G. Fabbri, *Rend. Accad. Naz. Lincei Class. Sci. fis. mat. nat. Ser. VIII*, **22**, 402 (1957); (d) P. Chiorboli, *Ricerca Scientifica, Suppl.*, 1 (1958); (e) L. H. Jones, *J. Chem. Phys.*, **29**, 463 (1958); (f) A. Hidalgo and J. P. Mathieu, *Compt. rend.*, **249**, 233 (1959). Preliminary X-ray work also lends credence to this supposition. See (g) E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 775 (1936); and (h) E. Staritzky and F. H. Ellinger, *Anal. Chem.*, **28**, 422, 423 (1956).

(19) J. Brigando, *Bull. soc. chim. France*, **4**, 503 (1957).

(20) E. A. Simpson and G. N. Waind, *J. Chem. Soc.*, 1748 (1958).

arising from the π^*-antibonding orbitals of the free cyanide ions.²¹ Thus, the energy level arrangement assumed for the tetrahedral cyanides is essentially the same as that previously used for the chromate, permanganate, manganate, ferrate, etc. anions (at least in so far as the *unfilled* orbitals are concerned).⁹

The spectra of the tetracoördinated and dicoördinated d¹⁰-transition metal cyanide complexes are then assigned as (recall Fig. 2a, b, c)

$^1A_1$: [core](e*)⁴(t₂**)⁶ $\longrightarrow$ [core](e*)⁴(t₂**)⁵(a₁*)¹: $^{1,3}T_2$

$^1A_1$: [core](e*)⁴(t₂**)⁶ $\longrightarrow$ [core](e*)⁴(t₂**)⁵(t₂**)¹: $^{1,3}A_1$ + $^{1,3}E$ + $^{1,3}T_1$ + $^{1,3}T_2$

$^1\Sigma_g^+$: [core](δg)⁴(πg*)⁴(σg⁺*)² $\longrightarrow$ [core](δg⁴)(πg*)⁴(σg⁺*)¹(σg⁺**)¹: $^{1,3}\Sigma_g^+$

$^1\Sigma_g^+$: [core](δg)⁴(πg*)⁴(σg⁺*)² $\longrightarrow$ [core](δg)⁴(πg*)³(σg⁺*)²(σg⁺**)¹: $^{1,3}\Pi_g$

$^1\Sigma_g^+$: [core](δg)⁴(πg*)⁴(σg⁺*)² $\longrightarrow$ [core](δg)⁴(πg*)⁴(σg*)¹(πu*)¹: $^{1,3}\Pi_u$

$^1\Sigma_g^+$: [core](δg)⁴(πg*)⁴(σg⁺*)² $\longrightarrow$ [core](δg)⁴(πg*)⁴(σg⁺*)¹(σu⁺*)¹: $^{1,3}\Sigma_u^+$

These optical jumps give rise to ten levels, $^{1,3}A_1$ + $^{1,3}E$ + $^{1,3}T_1$ + $2^{1,3}T_2$, for the tetracoördinated complexes, composed equally of five singlets and five triplets; and eight levels, $^{1,3}\Sigma_g^+$ + $^{1,3}\Pi_g$ + $^{1,3}\Pi_u$ + $^{1,3}\Sigma_u^+$, for the dicoördinated complexes, composed evenly of four singlets and four triplets. It is conceivable that additional dicoördinated transitions, such as the $\pi_g^* \rightarrow \pi_u^*,\ \sigma_u^*$ transitions (which give rise to the eight levels $^{1,3}\Sigma_u^+$ + $^{1,3}\Sigma_u^-$ + $^{1,3}\Pi_u$ and $^{1,3}\Pi_u$, respectively), may also enter into the detailed spectral assignment. As only the electronic hops $^1A_1 \rightarrow\ ^1T_2$ and $^1\Sigma_g^+ \rightarrow\ ^1\Sigma_u^+,\ ^1\Pi_u$ are electronically allowed, we assign the two strongest bands of the tetrahedral and digonal cyanide spectra to this source. The assignation of the weaker vibronically allowed absorptions is ambiguous without further experimental vibrational analysis of the electronic bands or without more precise theoretical estimates of the relative energetic locations of the various molecular orbital levels. From Fig. 1a, b, c, d and Table I we see that, at present, both the requisite

(21) As the internal $\pi \rightarrow \pi^*$ transition of the free cyanide anion is usually found around 185 mμ experimentally, the intense bands observed at wave lengths greater than 185 mμ in the transition metal cyanide complexes must arise from charge transfer processes. Hence, the antibonding molecular orbitals originating from the π^*-antibonding orbitals of the free cyanide groups must lie at higher energies than those originating from the free cyanide π-bonding and σ-lone pair oribtals pictured in Fig. 2a,b,c. For additional discussion of the location of the π^*-antibonding cyanide orbitals read ref. 6 and A. D. Walsh, *J. Chem. Soc.*, 2291 (1953).

Figure 2a

Figure 2b

Figure 2c

Fig. 2a, b, c.—Schematic molecular orbital energy level diagrams for tetrahedral and digonal transition metal compounds. Figures 2a, c illustrate the general molecular orbital level picture for tetrahedral [Figure 2a] and digonal [Figure 2c] compounds inclusive of π-bonding, and Figure 2b the correlation of the tetrahedral (T_d), square planar (D_4h), and skewed tetrahedral (C_s) "d" orbital molecular energy levels. Notice that the coördinate axes x and y of Figures 2a, b as here defined, bisect the ligand-metal-ligand bond angle.[39]

Fig. 3.—The dodecahedral (skewed double bisphenoid) disposition of the molybdenum(IV) octacyanide complex anion, according to Hoard and Nordsieck.[23]

theoretical and experimental precision is lacking, and that, therefore, only a rough qualitative spectral assignment is as yet possible.

The One Electron or Hole Configurations.—There exist no well singularized (both chemically and physically) transition metal cyanide compounds with a d^9-electron configuration, and the sole adequately documented examples of the d^1-configuration are the eight-coördinated $Mo(CN)_8^{-3}$, $W(CN)_8^{-3}$ and $Re(CN)_8^{-2}$ complex anions.[22] An X-ray structural determination has been performed for $K_4Mo(CN)_8 \cdot 2H_2O$ by Hoard and Nordsieck,[23] and in Fig. 3 we reproduce their geom-

(22) Recently a six-coördinated d^1-complex cyanide, $K_3Ti(CN)_6$, has been prepared and particularized by H. L. Schlafer and R. Gotz, *Z. anorg. allgem, Chem.*, **309**, 104 (1961). Its spectrum shows the characteristic Ti(III) ligand field absorption pattern: a single double humped peak at ~20,000 cm.$^{-1}$, with a hump separation of ~3400 cm.$^{-1}$ [this separation is in good qualitative agreement with the estimates of Jahn–Teller Ti(III) cleavages by A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (*N. Y.*), **3**, 304 (1958)]. The complex $K_2V(CN)_6$, which has been mentioned in the literature [read as an instance, Al. Yakimach, *Compt. rend.*, **191**, 789 (1930)] apparently is of doubtful reality.

etry. Mark that the only symmetry element possessed by the $Mo(CN)_8^{-4}$ anion is a single mirror plane, and hence that this anion belongs to the point group C_s. Hoard and Nordsieck have pointed out, however, that if all the Mo–C and C–N bond distances and angles are

(23) J. L. Hoard and H. H. Nordsieck, *J. Am. Chem. Soc.*, **61**, 2853 (1939).
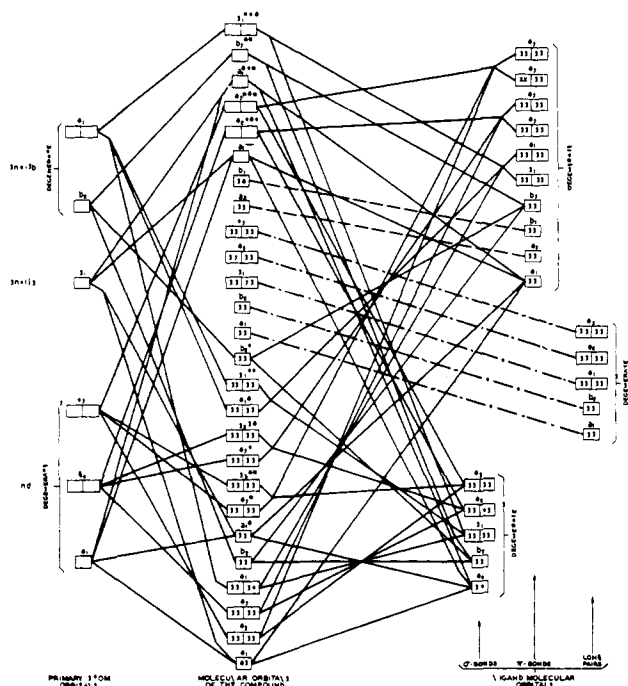
Fig. 4.—Schematic molecular orbital energy level diagram for an Archimedean antiprismatic (D_{4d}) transition metal compound [$e.g.$, the octafluorotantalate(V) anion]. The coördinate system chosen is as pictured in Figure 6a. The Archimedean antiprism is the structure favored by Stammreich and Sala[25c] for the free octacyanomolybdate(IV) anion.

averaged, the symmetry of the anion can be closely approximated by the point group D_{2d}. The isomorphism of crystals of $K_4W(CN)_8\cdot 2H_2O$ and $K_4Mo(CN)_8\cdot 2H_2O$ indicates that the related $W(CN)_8{}^{-4}$ anion is also of a similar structure.[23,24] Unfortunately no structural data are as yet available for the ions of prime concern in this paragraph, $Mo(CN)_8{}^{-3}$, $W(CN)_8{}^{-3}$ and $Re(CN)_8{}^{-2}$. However, it has been postulated that the very similar intensity and peak frequency distributions found in the infrared for *all* the molybdenum and tungsten octacyanides requires that these cyanides have identical structural forms.[18f,25] We shall here assume

(24) H. Gaadsgaard and W. D. Treadwell, *Helv. Chim. Acta*, **38**, 1669 (1955).

(25) (a) G. B. Bonino and G. Fabbri, *Rend. Accad. Naz. Lincei Class. Sci. fis. mat. nat. Ser. VIII*, **20**, 566 (1956); (b) E. G. Brame, Jr., F. A. Johnson, E. M. Larsen and V. W. Meloche, *J. Inorg. Nucl. Chem.*, **6**, 99 (1958). For a dissenting view (D_4d) see (c) H. Stammreich and O. Sala, *Z. Elektrochem.*, **65**, 149 (1961). [Latterly, E. König (d) *Theor. Chem. Acta*, 1, 23 (1962), has interpreted the spectra of the free d^1,[2] molybdo- and tungsto-octacyano anions in terms of this dissenting (antiprismatic) view. He obtains an excellent numerical fit of the observed bands (his observations agree well with ours) by means of the crystal field computations of M. Randić (for d^1-systems, (e) *Croat. Chem. Acta*, **32**, 189 (1960)) and G. Gliemann (for $d^{1,2}$-systems, (f) *Theor. Chem. Acta*, 1, 14 (1962)). However, this fit, upon close examination, exhibits several difficulties. First, it positions two levels, a triplet and a singlet, in a region of the infrared (at ~2000 and ~9500 cm.⁻¹, respectively) where no absorption occurs. Second, it assigns the strongest optical absorptions as highly forbidden two-electron jumps and, third, it predicts a temperature-dependent paramagnetism (due to thermal occupation of the low triplet level; *cf.* ref. 30) for the diamagnetic d^2-cyano complexes. Because of these difficulties, we feel that the antiprismatic structure for the free octacyano complex anions has not yet been established. Indeed, the store of evidence seems to indicate that the Hoard and Nordsieck[23] structure is the general one for eight coördination, and that the Archimedean antiprism is the exception. Study (g) J. L. Hoard, G. L. Glen and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 4293 (1961); (h) J. L. Hoard, J. V. Silverton, G. L. Glen and E. Willstadter, Proc. Seventh International Conference on Coördination Chemistry, Stockholm, Sweden, June, 1962; and (i) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962). The single electron electrostatic crystal field level order derived by these latter authors (and also derived independently by M. Randić, *J. Chem. Phys.*, **36**, 2094 (1962)) differs from our more general ligand field order. This difference arises because of their (quite proper) disregard of π-bonding effects.
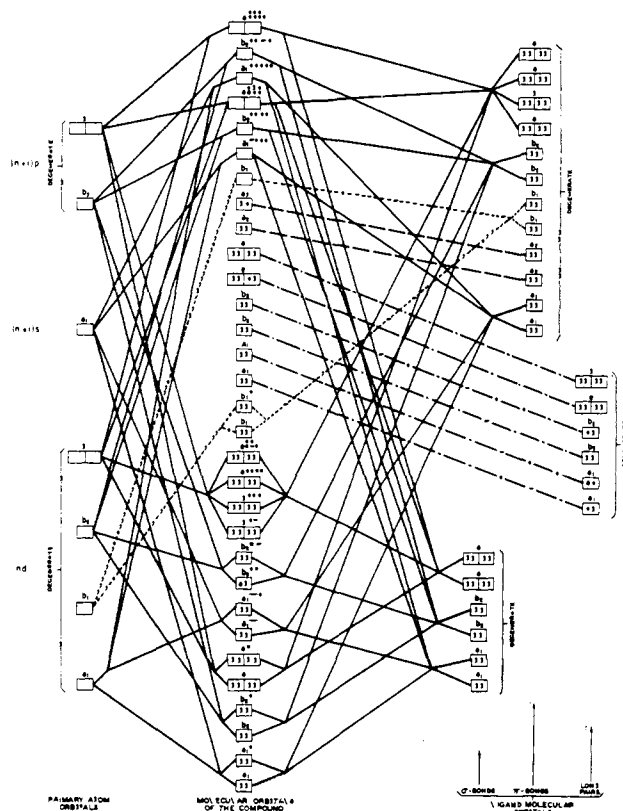
Fig. 5.—Schematic molecular orbital energy level diagram for a double bisphenoid (D_{2d}) transition metal compound. The coördinate system selected is as depicted in Figure 6b.[39]

that this postulate is true, and that in all cases we are dealing with the molecular point group C_s.[23]

In Fig. 4 and 5 are given, in schematic fashion, the molecular orbital energy levels for an eight-coördinated antiprism (D_{4d}) and a double bisphenoid (D_{2d}), respectively [the analogous figure for the eight-coordinated cube (O_h)[25j] can be found in ref. 3f]. And in Fig. 6a,b we show how these diagrams are interrelated to the cube and to the C_s-geometry of Hoard and Nordsieck. We omit, for convenience, in Fig. 6a,b the filled bonding and non-bonding levels of Fig. 4 and 5 as well as the high lying empty antibonding $(n + 1)s$- and $(n + 1)p$-like levels. No loss in discussional generality is thereby incurred, as we have not been able to identify transitions from or to such levels in our studies.[26] It is to be noted that the effect of the

Historically, the cubical (O_h) form was first postulated for these anions (j) W. G. Penney and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1363 (1937), and molecular orbital, valence bond and crystal field treatments made on this basis. But, more modernly, computations have all been based (with the above noted exceptions) on the experiments of Hoard and Nordsieck.[23] Peruse (k) G. E. Kinball, *J. Chem. Phys.*, **8**, 188 (1940); (l) G. Racah, *ibid.*, **11**, 214 (1943); (m) B. Higman, *ibid.*, **21**, 2224 (1953) (wrongly corrects Kimball); and (n) J. C. Eisenstein, *ibid.*, **25**, 142 (1956). Directed valence bond hybrid orbitals for the (D_{2d}) Hoard and Nordsieck[23] structure were constructed by Racah,[25l] those for the (D_{4d}) antiprismatic structure by Racah[25l] and G. H. Duffey (*J. Chem. Phys.*, **18**, 746 (1950)), and those for the cube by J. H. Macek and G. H. Duffey (*ibid.*, **34**, 682 (1961)).

(26) The relative ordering of these levels may be theoretically rationalized as follows. We start from the cube (O_h). On going from the cube to the antiprism (D_{4d}), we note that the σ-bonding power of an xz,yz-type orbital increases relative to that of an xy-type orbital. Hence, the molecular orbital $e_3(xz,yz)$ must antibond more than the molecular orbital $e_2(xy,x^2-y^2)$, which in turn must antibond more than the molecular orbital $a_1(z^2)$. Similarly, we find that on going from the cube to the double bisphenoid (D_{2d}), more e-type ligand molecular orbitals are created to bond to the metal $d_{xz,yz}$ orbitals than b_2-type ligand molecular orbitals are created to bond with the d_{xy} metal orbitals. Therefore, we come to expect that the $e(xz,yz)$ molecular orbital will be more antibonding than the corresponding $b_2(xy)$ molecular orbital. In addition, since overlap considerations tell us that $b_2(xy)$ will be both strongly σ- and π-antibonding while $a_1(z^2)$ is strongly π-antibonding and weakly σ-antibonding, and $b_1(x^2-y^2)$ is only π-antibonding,
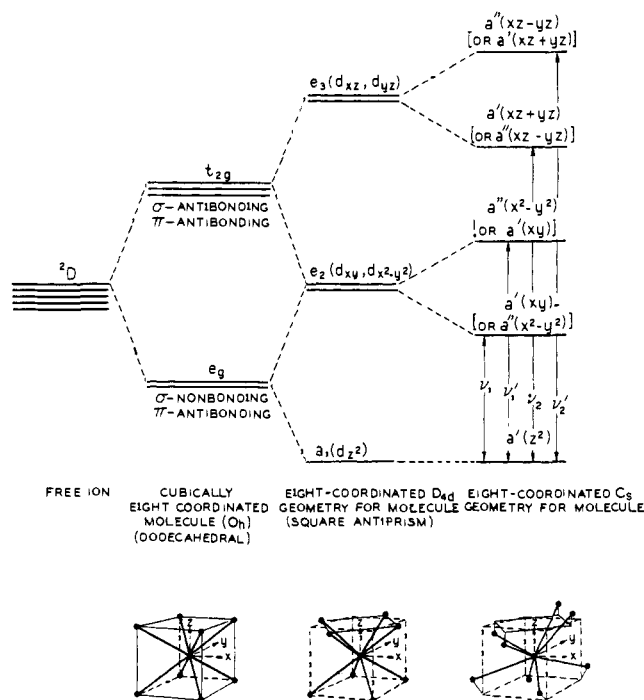
Fig. 6a.—Correlation of the cubic (O_h), Archimedean antiprismatic (D_{4d}), and skewed Archimedean antiprismatic (C_s) "d" orbital molecular energy levels.

reduction in regularity from D_{2d} (or D_{4d}) to C_s is to segregate the doubly degenerate e-level into two non-degenerate a-levels. Therefore, we predict that an octacoördinated d^1-complex of C_s-eurythmy should manifest *four* "d–d" type ligand field bands. It is obvious from Fig. 7a, b and Table II that this prediction is substantiated.

TABLE II

SPECTRAL DATA FOR THE d^1-TRANSITION METAL CYANIDE COMPLEX ANIONS

λ_{max}, mμ	ν_{max}, cm.$^{-1}$	ϵ_{max}	$f \times 10^{-4}$	Assignment	Calcd. frequency, cm.$^{-1}$
				$Mo(CN)_8{}^{-3}$	
387.7	25,800	1350	202	$^2B_1 \rightarrow {}^2B_2$	Fitted
312.5	32,000	800	219	$^2B_1 \rightarrow {}^2A_1$	Fitted
271.7	36,800	2000	386	$^2B_1 \rightarrow {}^2E$	Fitted
251.3	39,800	1900	350		
				$W(CN)_8{}^{-3}$	
357.0	28,010	1790	281	$^2B_1 \rightarrow {}^2B_2$	Fitted
296.8	33,700	810	221	$^2B_1 \rightarrow {}^2A_1$	Fitted
259.0	38,600	2120	364	$^2B_1 \rightarrow {}^2E$	Fitted
239.2	41,800	2170	351		

The relatively high intensity of these octacoördinate "d–d" transitions furnishes conclusive proof of their non-centrosymmetric structure. The absorptions are thus best viewed as tetrahedral-like rather than octahedral-like.[27,28]

we divine that the $b_2(xy)$ molecular orbital will be more antibonding than the $a_1(z^2)$ molecular orbital which in turn will be more antibonding than the $b_1(x^2 - y^2)$ molecular orbital. A continuation of such cerebral processes yields the desired qualitative level placements [view Fig. 2a, b, 4, 5, 6a, b, 8, 10a, b].

(27) Due to the inherent instability of the $Re(CN)_8{}^{-3}$ anion, its spectrum could only be taken from a KBr mull of the salt $[Co(NH_3)_6]_2[Re(CN)_8]_3$. The spectrum showed a continuously increasing absorption as the ultraviolet was approached with no peaks in the region accessible to our instruments [a slight hump occurs ~20,000 cm.$^{-1}$ which is most probably due to the Co-$(NH_3)_6{}^{+3}$ cation]. With such poor spectral data and technique no conclusions of theoretical or experimental import could be reached for this particular compound.
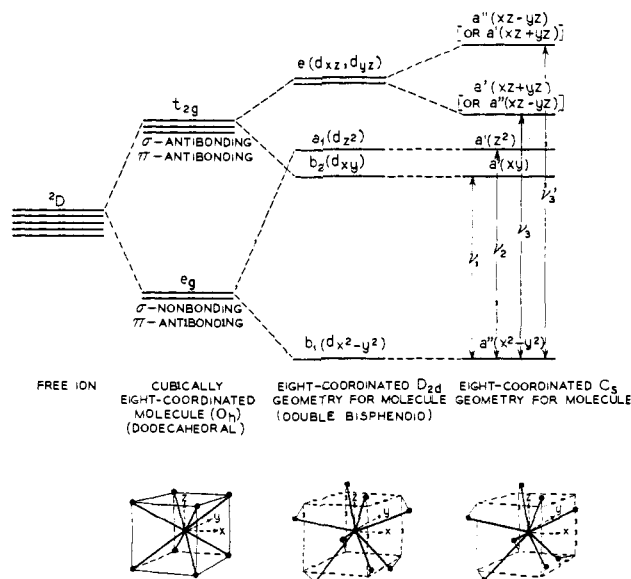

Fig. 6b.—Correlation of the cubic (O_h), double bisphenoidal (D_{2d}), and skewed double bisphenoidal (C_s) "d" orbital molecular energy levels.

The Two Electron or Hole Configurations.—All the known cyanide complexes of d^2-electronic configuration are eight coördinated with the exception of the six-coördinated trivalent vanadium complex. The octacyanides are $Mo(CN)_8{}^{-4}$, $W(CN)_8{}^{-4}$ and $Re(CN)_8{}^{-3}$. For these eight-coördinated anions we assume a *one electron* molecular orbital energy level pattern *identical* to that observed for the appositive d^1-anions. The ground electronic state for all these anions will then become $[b_1 \text{ or } a''(x^2 - y^2)]^2$ (see Fig. 6a, b); hence the diamagnetism of the complexes.[13,29] Then, taking into account only the single electron jumps, we may write the appropriate two-electron wave functions of the excited states as (for simplicity, we have here used the notation of the D_{2d} idealized geometry. From Fig. 6b it is apparent that no loss of generality is thereby incurred if one remembers that in the actual C_s geometry the e-type levels split).[30]

$$^1A_2 = 2^{-1/2}\{ |b_1\bar{b}_2| - |\bar{b}_1b_2| \}$$
$$^3A_2 = |b_1b_2|$$
$$^1B_1 = 2^{-1/2}\{ |b_1\bar{a}_1| - |\bar{b}_1a_1| \}$$
$$^3B_1 = |b_1a_1|$$
$$^1E = 2^{-1/2}\{ |b_1\bar{e}| - |\bar{b}_1e| \}$$
$$^3E = |b_1e| \tag{1}$$

Equations 1 foretell the following excitation energies for the d^2-octacoördinated cyanides (perceive also Fig. 8).

(28) It is of interest to mention that with the D_{2d} structural approximation of Hoard and Nordsieck[?] not all the octacyanide electronic transitions are symmetry allowed. As an instance, the d^1- and d^2-optical leaps $^2B_1 \rightarrow$ $^2A_1$, $^2B_2$ and $^1A_1 \rightarrow {}^1A_2$, $^1B_1$, serially, are electronically forbidden within D_{2d}. Of course, within the actual C_s-geometrical disposition all transitions are symmetry allowed.

(29) (a) J. H. E. Griffiths, J. Owen and I. M. Ward, *Proc. Roy. Soc.* (London), **219A**, 526 (1953); (b) W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936).

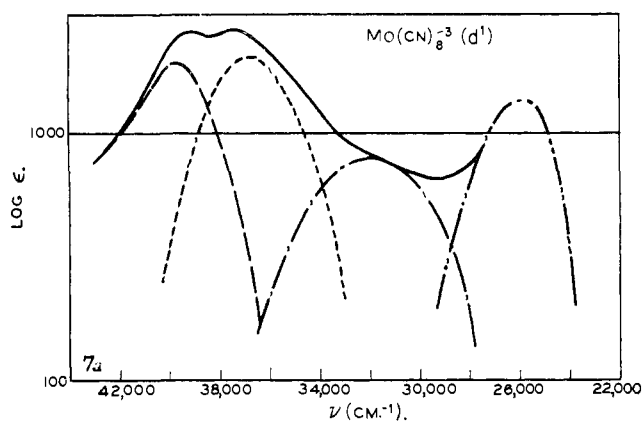(30) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

SPECTRA OF d^1 COMPLEXES:

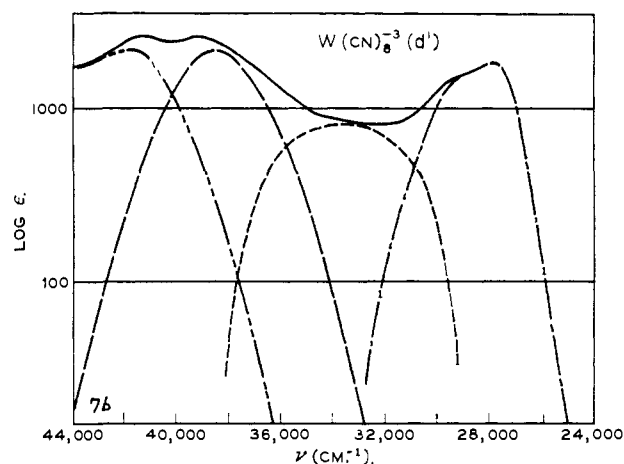| ν	ASSIGNMENT	$Mo(CN)_8{}^{-3}$	$W(CN)_8{}^{-3}$
ν_1	Δ_1 $(b_1 \rightarrow b_2)$	25,800 cm.$^{-1}$	28,010 cm.$^{-1}$
ν_2	Δ_2 $(b_1 \rightarrow a_1)$	32,000 "	33,700 "
ν_3	Δ_3 $(b_1 \rightarrow e)$	36,800 "	38,600 "
ν_3'	$\Delta_3 + \delta$ $(b_1 \rightarrow e')$	39,800 "	41,800 "

Figure 7a

Figure 7b

Fig. 7a, b.—The absorption spectra of the d^1 octacoördinate transition metal cyanide complex anions.   Figure 7a pens the spectrum of the molybdenum(V) complex and Figure 7b the spectrum of the tungsten(V) complex.

$$\nu_1(^1A_1 \rightarrow {}^3A_2) = \Delta_1 - 105F_4$$
$$\nu_2(^1A_1 \rightarrow {}^3B_1) = \Delta_2 - (12F_2 + 45F_4)$$
$$\nu_3(^1A_1 \rightarrow {}^3E) = \Delta_3 - (9F_2 + 60F_4)$$
$$\nu_3'(^1A_1 \rightarrow {}^3E') = (\Delta_3 + \delta) - (9F_2 + 60F_4)$$
$$\nu_4(^1A_1 \rightarrow {}^1A_2) = \Delta_1 - 35F_4$$
$$\nu_5(^1A_1 \rightarrow {}^1B_1) = \Delta_2 - (4F_2 + 15F_4)$$
$$\nu_6(^1A_1 \rightarrow {}^1E) = \Delta_3 - (3F_2 + 20F_4)$$
$$\nu_6'(^1A_1 \rightarrow {}^1E') = (\Delta_3 + \delta) - (3F_2 + 20F_4) \qquad (2)$$

where the quantities F_k ($k = 2,4$), are the well-known Slater–Condon–Shortley[31] parameters, and the Δ_k and δ ($k = 1,2,3$), are the one-electron molecular orbital energies of Fig. 6b and Table II.[32]

The spectra of the octacoördinated d^2-cyanide anions are displayed in Fig. 9a, b, c, and the accompanying spectral data and assignments in Table III. We see that the use of a reasonable ratio of F_2:F_4 of about ten, together with the Δ_k and δ ($k = 1,2,3$), values gleaned from the appositive d^1-systems, yields a quite gratifying agreement between theory and experiment.[33]

(31) (a) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, Cambridge, 1953; (b) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. 1 and 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(32) Since the observed solution spectra are so broad, we have omitted in our computations all spin-orbit and second-order configuration interactions (these latter interactions arise from the descent from the artificial D_{2d}-geometry to the actual C_8-geometry). Such refinements produce experimentally undetectable alterations in the predicted energy level disposition under our experimental conditions. It is important to keep in mind, however, that it is only by virtue of such interactions that the bands which are orbitally (in D_{2d}) or spin-orbitally (in D_{2d} or C_8) forbidden become electronically allowed. Hence, for the rationalization of the observed intensity patterns such interactions are of great consequence.

(33) As no data on the free ion spectrum of $Re(CN)_8{}^{-2}$ could be obtained, there were no means available to assess Δ_k and δ, ($k = 1, 2, 3$) for $Re(CN)_8{}^{-3}$. Therefore, the next best thing was done: the spin-allowed bands were fitted and from this base the spin-forbidden bands predicted. From Table III the agreement is seen to be satisfactory. Please note that there exist more electron correlation integrals in ligand field theory than just the two utilized here, F_2 and F_4 (or equivalently, B and C). Indeed, for cubical geometries there are actually ten such integrals (systems of lower structural regularity naturally have larger numbers of correlation integrals).[3b] Hence, a significant approximation (and simplification) has already been made in the assumption of but two independent correlation parameters, and the additional assumption of a mathematical connection between these two parameters further compounds the approximation. It is of interest to witness in this conjunction that a reduction in magnitude of the electron correlation integrals cannot always be interpreted as a manifestation of covalent linkages. As an example, we compare the F_2, F_4, B and C values of the fluorides (ionic case) with those of the cyanides (covalent case). The fluorides have F_2 equal to ~$14F_4$ and C equal to ~$3.9B$, with F_4 equal to ~70 cm.$^{-1}$, and B equal to ~630 cm.$^{-1}$ (A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* [*N. Y.*], **6**, 134 (1959)). The cyanides have F_2 equal to ~$10F_4$ and C equal to ~$7B$, with F_4 equal to ~100 cm.$^{-1}$ and B equal to ~500 cm.$^{-1}$. Thus, for these two systems, F_2 remains essentially invariant, F_4 and C increase, and B decreases with increased covalency. It is therefore difficult to

ONE—ELECTRON MOLECULAR ORBITAL ENERGY LEVEL (O_{2d}) SCHEME NEGLECTING ELECTRON—ELECTRON REPULSIONS

ONE—ELECTRON MOLECULAR ORBITAL ENERGY LEVEL (O_{2d}) SCHEME WITH ELECTRON—ELECTRON REPULSION
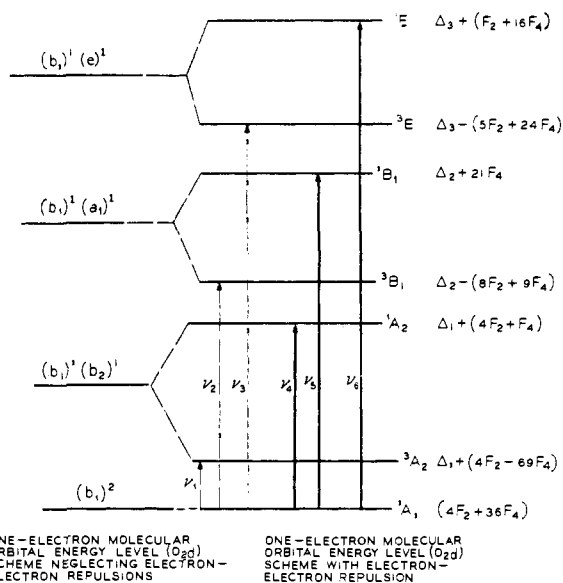
Fig. 8.   The single "d" orbital excitations permitted a d^2 octacoördinated transition metal cyanide complex anion.

reconcile, in any direct manner, elementary covalency concepts with sophisticated ligand field results (for more discussion of this point read A. D. Liehr, J. Ferguson and D. L. Wood, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, Columbus, Ohio, June, 1962, and *J. Phys. Chem.*, submitted.

We should also mention that we have omitted from our octacyano spectral considerations electron configurations which arise from two electron promotions. This omission was based upon the rather remote spectral location (in the charge transfer region) of such promoted states, and their associated relatively weak absorption probabilities. (The remoteness of these double promotions stems from our choice of an over-all "d–d" separation of ~39,000 cm.$^{-1}$ for pentavalent molybdenum and tungsten (notice that this choice implies that trivalent molybdenum and tungsten cyanides should have an over-all "d–d" separation of ~19,000-25,000 cm.$^{-1}$ if the familiar 20–30% reduction of over-all "d–d" separation per unit decrement in ionization number is followed. There is some question as to the validity of a simple reduction rule of this sort for covalent complexes of the cyanide ilk. We have not used this reduction in our fit of the quadrivalent spectra of the molybdenum, tungsten and rhenium octacyanides. If this reduction were used, the values of F_2 and F_4 here reported would be altered somewhat. That some such alteration of this type is really required can be seen from the somewhat large variance of the molybdenum and tungsten F_4 values listed in Table III.)) In the alternate spectral assignment of König,[25d] these promotions are not omitted. König, who assumes an over-all "d–d" split of ~25,000 and ~50,000 cm.$^{-1}$ for quadrivalent and pentavalent molybdenum and tungsten, serially, needs these double promotions to numerically fit the observed bands. Thus, he assigns absorptions to (D_{4d}) electron configurations of the kind $(e_2)^2 = {}^1A_1 + {}^3A_2 + {}^1B_1 + {}^1B_2$, $(e_2)^1(e_3)^1 = {}^{1,3}E_1 + {}^{1,2}E_3$, and $(e_3)^2 = {}^1A_1 + {}^3A_2 + {}^1E_2$, which we have neglected (For D_{4d} configurations only the transitions $^1A_1 \rightarrow {}^1B_2$, $^1E_1$ are spin-orbitally allowed). The determination of the singlet or triplet character of the electronic states in-
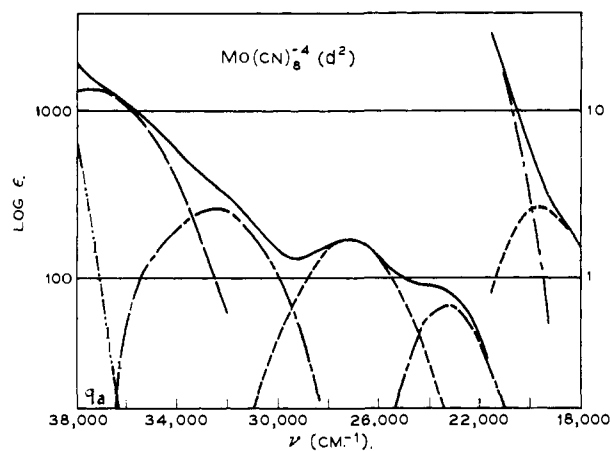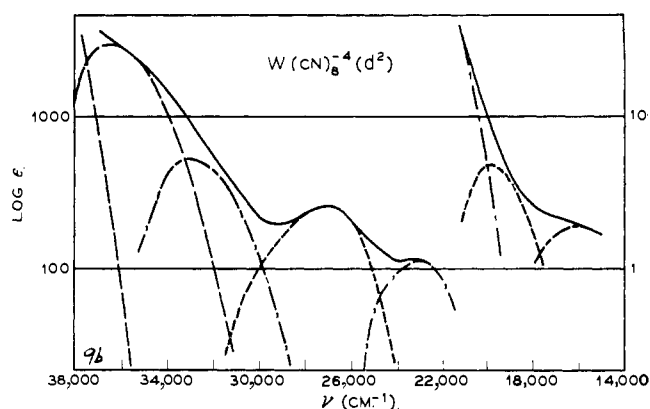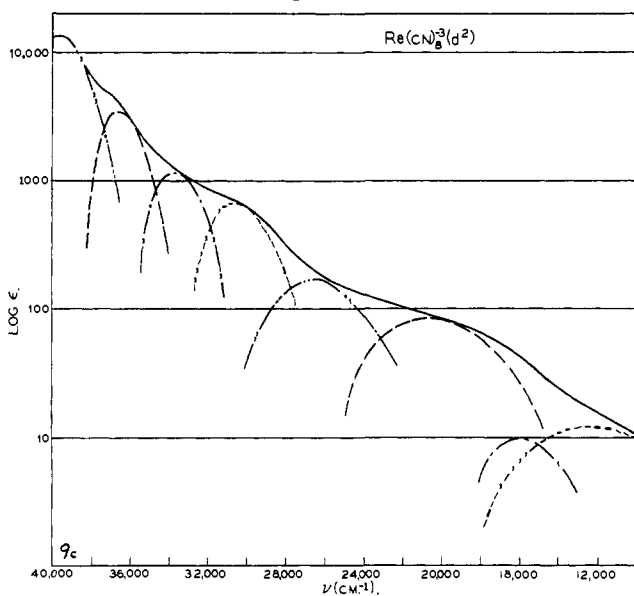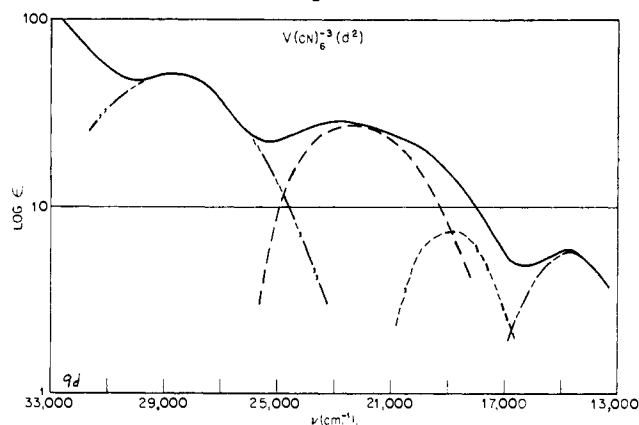
Figure 9a

Figure 9b

Figure 9c

Figure 9d

Fig. 9a, b, c, d.—The absorption spectra of the d^2-transition metal cyanide complex anions. Figure 9a graphs the spectrum of the molybdenum(IV) complex, Fig. 9b the spectrum of the tungsten(IV) complex, Fig. 9c the spectrum of the rhenium(V) complex, and Fig. 9d the spectrum of the vanadium(III) complex.

Our results to date for the hexacoördinated vanadium d^2-complex have been somewhat disappointing. The major difficulty is preparative: the problem of obtaining an uncontaminated solution of the $V(CN)_6^{-3}$ anion. Nearly a dozen preparations were attempted but all seem to be contaminated in one way or another. Our *tentative* results are given in Fig. 9d and Table IV. They lead to an octahedral Δ-value of 23,390 cm.$^{-1}$ and a Racah B-value (equals $F_2 - 5F_4$) of 506 cm.$^{-1}$ (in

duced by the multiple occupancy of the degenerate orbitals is easily accomplished if one but notes that the exclusion principle requires that these states, whether singlet or triplet, be completely antisymmetric under exchange of electrons. Hence, as the singlet and triplet spin functions are separately antisymmetrical and symmetrical under such exchanges they can only be associated with orbital product functions which are serially symmetrical and antisymmetrical. The symmetries of these orbital product functions are readily enumerated by an inspection of the species generated by their symmetrical (symbolized by { }) and antisymmetrical (symbolized by [ ]) group theoretic direct products (*e.g.*, {e_1^2 or s} = $A_1 + E_2$ and {e_2^2} = $A_1 + B_1 + B_2$ (singlets), and [e_1^2 or s] = A_2 and [e_2^2] = A_2 (triplets))). It must be emphasized that unreasonable values of F_2 are obtained (F_2 for tungsten becomes twice that for molybdenum) and not all bands are assigned, if a fit is attempted for the antiprismatic (D_{4d}) symmetry without the inclusion of these double promotions. Hence, no resolution of the theoretical dilemma for the antiprismatic structure can be accomplished by waiver of double promotions. One last remark is not out of place. Mark that the ligand field treatment of cyanide complexes, as outlined above, requires no double-talk of the back donation variety to rationalize the resultant electronic charge distributions. (In ligand field theory back donation, *per se*, only occurs whenever the highly positioned empty π^*-cyanide anion antibonding molecular orbitals participate strongly in complex formation.)

terms of our notation of Table III where $F_2 = 10F_4$, this magnitude for B implies that $B = 5F_4 = 506$ cm.$^{-1}$ or $F_2 = 10F_4 = 1012$ cm.$^{-1}$). However, this value of B presages that the first and second spin-forbidden bands, $^3T_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$ and $^3T_{1g} \rightarrow {}^1A_{1g}$, respectively, should lie at $\sim10,350$ cm.$^{-1}$ ($\sim20B$) and 20,117 cm.$^{-1}$ ($\sim40B$). It is difficult to reconcile simultaneously, the observed bands at 14,700 and 18,870 cm.$^{-1}$ with this prediction, unless drastically different magnitudes of the F_k ($k = 2,4$) are postulated for the singlet and triplet manifolds, separately. Perhaps these bands are spurious and due to contaminants. Further work is now in progress to help clarify this perplexing situation.

The only acceptably documented (both chemically and physically) representatives of d^8-transition metal cyanides are all of the form $M(CN)_4^{-1}$ or $M(CN)_4^{-2}$, where $M = Au(III)$ or $Ni(II)$, $Pd(II)$, and $Pt(II)$, respectively. These all have the square planar conformation.[15,34] In computing and assigning the observed spectra we have utilized the one-electron molec-

(34) H. Brasseur and A. de Rassentosse, *Bull. soc. France Min.*, **61**, 129 (1938). The quadrate planarity of the tetracyanoaurate(III) anion has not yet been established by a direct structural determination, but infrared observations intimate its presence. See (a) J. P. Mathieu and H. Poulet, *Compt. rend.*, **248**, 2315 (1959); (b) A. Hidalgo and J. P. Mathieu, *ibid.*, **249**, 233 (1959); and (c) *Anales Real. Soc. Españ. Fis. y Quim. (Madrid)*, **56A**, 9 (1960).
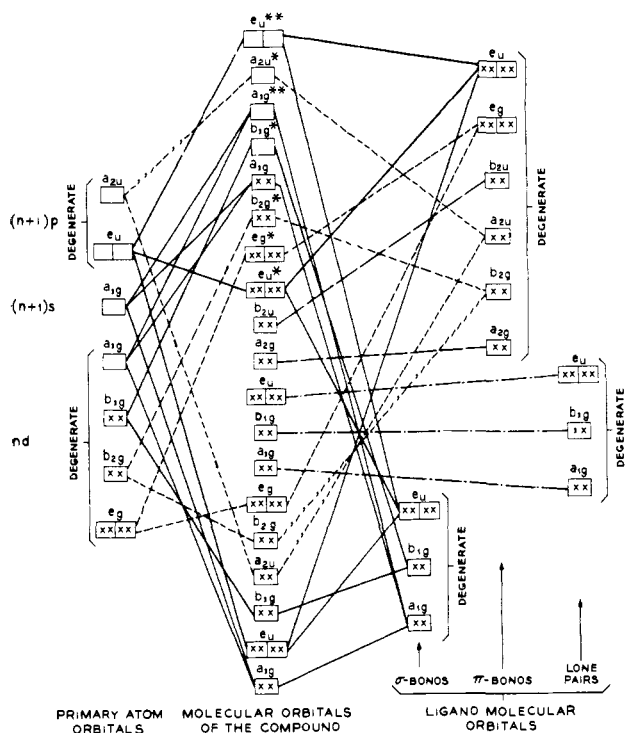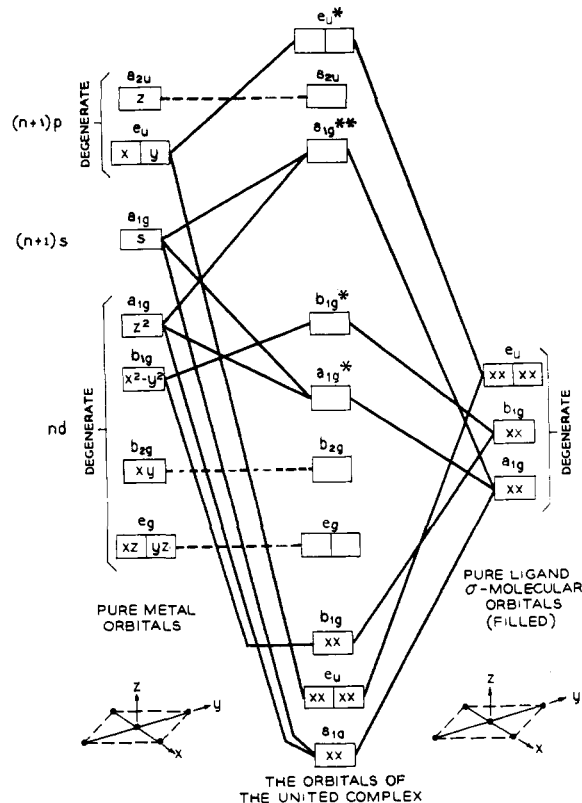
Figure 10a

Figure 10b

Fig. 10a, b.—Schematic molecular orbital energy level diagrams for a square planar transition metal compound. Figures 10a and 10b display the general molecular orbital level picture inclusive and exclusive of π-bonding, separately. Mark that the coördinate axes x and y are here directed along the metal-ligand bond.[39]

ular orbital scheme drawn in Fig. 10a, b and 2b. The location of the σ-antibonding $a_{1g}^*(z^2)$ molecular orbital level is to be especially noted. In contrast to other

TABLE III

SPECTRAL DATA FOR THE d^2-TRANSITION METAL CYANIDE COMPLEX ANIONS

λ_{max}, mμ	ν_{max}, cm.$^{-1}$	ϵ_{max}	$f \times 10^{-4}$	Assignment	Calcd. frequency, cm.$^{-1}$
				$Mo(CN)_8^{-4}$	
				$(F_2 = 10F_4 = 750$ cm.$^{-1})$	
...	....	..	..	$^1A_1 \rightarrow {}^3A_2$	17,925
510.0	19,600	2.7	0.41	$^1A_1 \rightarrow {}^3B_1$	19,625
431.0	23,200	69	9.4	$^1A_1 \rightarrow {}^1A_2$	23,175
...	....	..	..	$^1A_1 \rightarrow {}^3E$	25,550
...	....	..	..	$^1A_1 \rightarrow {}^3E'$	28,750
367.6	27,200	170	30.1	$^1A_1 \rightarrow {}^1B_1$	27,875
308.2	32,450	262	55.7	$^1A_1 \rightarrow {}^1E$	33,050
267.4	37,400	1,350	244	$^1A_1 \rightarrow {}^1E'$	36,050
240.0	41,670	15,540	..	Charge transfer	
				$W(CN)_8^{-4}$	
				$(F_2 = 10F_4 = 1200$ cm.$^{-1})$	
...	....	..	..	$^1A_1 \rightarrow {}^3B_1$	13,900
625.0	16,000	1.9	0.35	$^1A_1 \rightarrow {}^3A_2$	15,410
502.4	19,900	4.8	0.59	$^1A_1 \rightarrow {}^3E$	20,600
...	....	..	..	$^1A_1 \rightarrow {}^3E'$	23,800
434.8	23,000	111.0	17.4	$^1A_1 \rightarrow {}^1A_2$	23,810
370.3	27,000	251.0	48.5	$^1A_1 \rightarrow {}^1B_1$	27,100
303.1	33,000	520	86.1 ⎫	$^1A_1 \rightarrow {}^1E$	32,600
273.7	36,500	3,000	471 ⎭		35,800
249.0	40,160	25,060	..	Charge transfer	
				$Re(CN)_8^{-3}$	
				$(F_2 = 10F_4 = 1000$ cm.$^{-1})$	
795	12,600	12	4.2	$^1A_1 \rightarrow {}^3A_2$	13,408
625	16,000	10	2.1	$^1A_1 \rightarrow {}^3B_1$	15,596

490	20,408	84	30	$^1A_1 \rightarrow {}^1A_2$	Fitted
...	....	..	..	$^1A_1 \rightarrow {}^3E$	20,675
...	....	..	..	$^1A_1 \rightarrow {}^3E'$	23,557
376	26,596	177	39	$^1A_1 \rightarrow {}^1B_1$	Fitted
326	30,675	653	107	$^1A_1 \rightarrow {}^1E$	Fitted
298	33,557	1,105	148	$^1A_1 \rightarrow {}^1E'$	Fitted
273	36,630	3,415	..	Charge transfer	
253	39,560	13,000	..	Charge transfer	

TABLE IV

SPECTRAL DATA (TENTATIVE) FOR THE d^2-TRANSITION METAL CYANIDE COMPLEX ANION, HEXACYANOVANADATE(III)

The band at 530 mμ appears in some samples only after Gaussian analysis, but in others as a distinct shoulder placed at 560 mμ. The intensities of all the bands vary within a 10 to 15% range in the samples measured.

λ_{max}, mμ	ν_{max}, cm.$^{-1}$	ϵ_{max}	$f \times 10^{-4}$	Assignment	Calcd. frequency, cm.$^{-1}$
				$V(CN)_6^{-3}$	
				$(F_2 = 10F_4 = 1012$ cm.$^{-1})$	
350	28,600	50.0	...	$^3T_{1g} \rightarrow {}^3T_{1g}$	Fitted
450	22,200	27.0	...	$^3T_{1g} \rightarrow {}^3T_{2g}$	Fitted
530	18,870	7.5	...	....	...
680	14,700	5.7	...	....	...
...	....	..	...	$^3T_{1g} \rightarrow {}^1A_{1g}$	20,117
...	....	..	...	$^3T_{1g} \rightarrow {}^1E_g$	10,380
				$^3T_{1g} \rightarrow {}^1T_{2g}$	10,310
				$Ti(CN)_6^{-3}$	
448.4	22,300^a	..	...	$^2T_{2g} \rightarrow {}^2E_g$	....
529.1	18,900^a	..	...		

^{a} Schlafer and Gotz.[22]

authors,[35,36] we find that this level must lie *between* the b_{2g}^* (xy) π-antibonding level and the b_{1g}^* ($x^2 - y^2$)

(35) Peruse, for example, (a) J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, 486 (1958), and (b) A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, **35**, 2206 (1961).
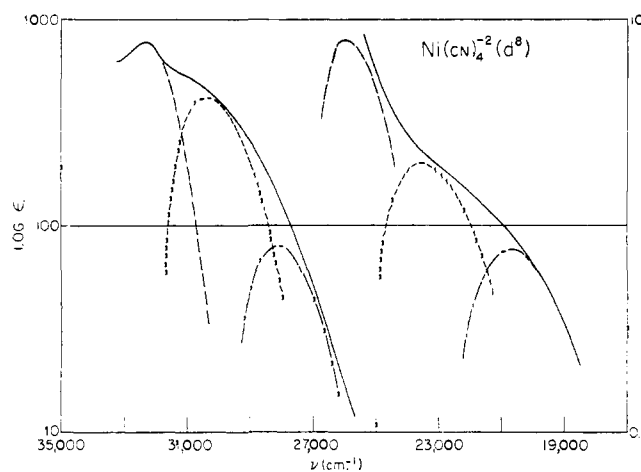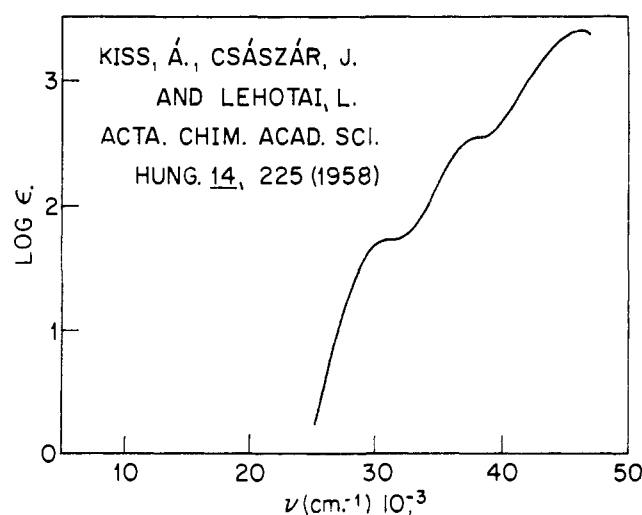
Figure 11a

λ_{MAX} (mμ)	ν_{MAX} (cm.$^{-1}$)	ϵ_{MAX}
217	46,083	2,400
264	37,879	331
323	30,960	51

Figure 11b

Fig. 11a, b.—The absorption spectrum of the d^8 tetracoördinated transition metal cyanide complex anions, tetracyanonickelate(1I) [Figure 11a] and tetracyanoaurate(III) [Figure 11b].

σ-antibonding level for any reasonable agreement to be obtained between the theoretical and experimental spectra. Note that this level sequence differs from that which would be obtained from those of the octacyanide complexes (Fig. 6b and 8), previously discussed, by changing the signs of all the octacyanide ligand field parameters, Δ_k, (k = 1,2,3). We believe that this latter difference is due primarily to solvation effects, and that, in the absence of these effects, the inverse octacyanide diagram would apply.[37]

The energy expressions for the square planar d^8-electronic system are essentially the same as those given previously (eq. 2 and Fig. 8) for the dodecahedral d^2-system (they would be exactly the same if the inverse dodecahedral one electron scheme applied here[38]). The

(36) "Exact" calculations by R. F. Fenske, D. S. Martin and K. Ruedenberg ["Symposium on Ligand Field Theory," 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961, and *Inorg. Chem.*, 1, 441 (1962)] for the platinum(II) tetrachloride anion and its derivatives place the a$_{1g}$*(z^2) level slightly lower, between the e$_g$*(xz,yz) and b$_{2g}$*(xy) π-antibonding levels. However, the relative closeness of the a$_{1g}$*(z^2) and b$_{2g}$*(xy) levels, as determined in this work (see text), and the certain presence of solvent perturbations in the nickel(II) tetracyanide solutions utilized here, in contrast to the lack of such perturbations in Fenske, Martin and Ruedenberg's platinum(II) tetrachloride solutions, may be taken as indicating substantial agreement between the (independent) semi-empirical d^8-computations reported in this paper and those of Fenske, Martin and Ruedenberg. This happenstance is most gratifying.

(37) The (square planar) inverse octacyanide level arrangement in which the *seemingly* unbound d$_{z2}$ orbital lies higher than the π-antibonding d$_{xz,yz}$ orbitals may be thought of as happening because of one of two independent mechanisms: (i) because of strong σ-bonding of the equatorial d$_{z2}$ bulge with the surrounding four equatorial ligands, and (ii) because of axial solvent perturbations. Fenske, Martin and Ruedenberg[36] believe that the former mechanism is most likely in the case of their tetracoördinated platinum(II) complexes. We have no way of assessing the relative importance of these two alternative mechanisms from our nickel(II) cyanide data. However, in the case of the octacyanides we definitely feel that it is the strong molecular orbital interactions which determine the relative placement of the a'(z^2) level (see Fig. 7b), and in the case of the planar tetracyanides, as stated in the text, we feel that the two mechanisms combine to yield the observed results, σ-bonding raising the a$_{1g}$*(z^2) level above the e$_g$*(xz,yz) level and solvent perturbations lifting it above the b$_{2g}$*(xy) level.

(38) To see this fact one need only notice that the eight-electron (or two-hole) level scheme for d-electrons is identical to the appositive two-electron scheme turned topsy-turvy, whenever similar covalency and solvent effects obtain for both electronic configurations. Then, since the point groups

expressions differ solely in the locale of the $^{1,3}A_2$ and $^{1,3}B_1$ levels. For the d^8-electronic system $\nu_3 > \nu_1 > \nu_2$ and $\nu_6 > \nu_4 > \nu_5$ in the notation of Fig. 8 and eq. 2. In the present context the one-electron molecular orbital assignments of Fig. 8 should now be interpreted as "one-hole" molecular orbital assignments.[38]

The spectra of the Ni(CN)$_4$$^{-2}$ and Au(CN)$_4$$^{-1}$ anions are shown in Fig. 11a, b. The data derived therefrom are epitomized in Table V, together with the data of Jørgensen[40] for the Pd(CN)$_4$$^{-2}$ and Pt(CN)$_4$$^{-2}$ anions.[41]

C$_{4v}$, D$_4$ and D$_{2d}$ (C$_{4v}$ and D$_4$ are subgroups of the complete D$_{4h}$ group) are isomorphous (*i.e.*, have the same symmetry labels[39]), and since the C$_{4v}$, D$_4$ and D$_{2d}$ geometries under consideration have mutually *inverse* one-electron molecular orbital level schemes, according to our previous stipulation (compare Fig. 5 and 6b with Fig. 2 of ref. 3f), the d^8-complexes of D$_{4h}$ geometry and the d^2-complexes of D$_{2d}$ geometry which meet our physical specifications will have *identical* energy level parades.

(39) The subscripts 1 and 2 of the square planar b-type molecular orbitals are somewhat arbitrary, and thus differ from author to author, or within a series of publications by the same author,[3f] dependent upon the coördinate system utilized. If the *x* and *y*-coördinates are chosen to *bisect* the ligand–metal–ligand bond angle, as in Fig. 2b, 5 and 6b and in Fig. 2 of ref. 3f, the orbital d$_{xy}$ obtains the label b$_{2g}$ and becomes the strongly σ-antibonding b$_{2g}$* level, while the d$_{x^2 - y^2}$ obtains the label b$_{1g}$ and becomes the strongly π-antibonding b$_{1g}$* level. On the other hand, if the *x* and *y* coördinates are chosen to lie *along* the metal–ligand bond, as in Fig. 10a, b, then it is the b$_{1g}$* (x^2 — y^2) level which becomes the strongly σ-antibonding level and the b$_{2g}$* (xy) level which becomes the strongly π-antibonding level. Thus, no physical import should be attached to the subscripts 1 and 2 if the coördinate system utilized is not given. [Another example of the use of an alternative coördinate system may be discovered on comparison of L. E. Orgel's (*J. Inorg. Nucl. Chem.*, 14, 136 (1960)) discussion of the ground electronic state of the octacyanides with that given in this article.]

(40) C. K. Jørgensen, "Absorption Spectra of Complexes of Heavy Metals," Report to the European Research Office, U. S. Department of the Army, Frankfurt am Main, under Contract No. DA91-508EUC-247, October, 1958.

(41) These data are in substantial agreement with those of other workers. Scan, *e.g.*, ref. 8 and (a) L. Szegö and P. Ostenelli, *Gazz. chim. ital.*, 60, 946 (1930); (b) A. Kiss, J. Csaszar and L. Lehotai, *Acta Chim. Acad. Sci. Hung.*, 14, 225 (1958); and (c) A. Kiss, J. Csaszar and E. Horvath, *ibid.*, 15, 151 (1958). The infrared absorption bands for the transition metal cyanides reported by these latter workers are spurious. No cyanide, to our knowledge, absorbs, either vibrationally or electronically, in the spectral range 4000 to 11,000 cm.$^{-1}$. An interpretation of the square planar d^8-cyanide spectra different from ours has lately been proposed by C. J. Ballhausen and H. B. Gray (to be published). Their interpretation bases itself upon an analysis of the square planar charge transfer spectra. In their view a$_{1g}$(z^2)

As in the case of the $Re(CN)_8^{-3}$ anion,[33] we have procured the semi-empirical parameters of the $Ni(CN)_4^{-2}$ anion, Δ_k ($k = 1,2,3$), from a theoretical fit of the spin-allowed bands (taking the ratio of $F_2:F_4$ to be eleven), and used these parameters to compute the positions of the spin-forbidden bands (as a check).[42] The agreement seems quite encouraging.[43]

Conclusion

It is evident from the foregoing that ligand field theory (that is, molecular orbital based crystal field theory[3f]) is quite successful in rationalizing the observed spectroscopic and magnetic properties of the d^n ($n = 0,1,2,8,9,10$) transition metal cyanide complexes. This situation is quite in contrast to the general viewpoint prevalent heretofore (with the exception of a few isolated outcries[4–8,29a]). It is to be hoped that the initial success obtained in this paper for an entire family of cyano compounds will be extensible in the future to other families of this same sort [e.g., the d^n cyanides (n

level is variable in the homologous series MX_4^{-2}, where M equals Ni, Pd and Pt. The energetic position of the $a_{1g}(z^2)$ level is imagined to vary from a location between the $b_{2g}(xy)$ and $e_g(xz;yz)$ [for Ni(II)] levels to one below the $e_g(xz,yz)$ levels [for Pt(II)]. Although intellectually stimulating, their interpretation cannot be regarded as final, as it is founded upon uncertain charge transfer assignations. [They have not been able to differentiate between the equally probable (and likely) bonded-antibonded, non-bonded-antibonded, and antibonded-antibonded charge transfer processes in these complexes (see Fig. 10a). As an instance of the importance of the bonded-antibonded processes read J. S. Griffith (*Mol. Phys.*, **3**, 477 (1960))].

(42) The one-electron Δ_k ($k = 1, 2, 3$) molecular orbital energies for the $Ni(CN)_4^{-2}$ anion thus derived have the values $\Delta_1[(x^2 - y^2) - z^2] = 32,140$ cm.$^{-1}$, $\Delta_2[(x- - y^2) - xy] = 32,760$ cm.$^{-1}$ and $\Delta_3[(x^2 - y^2) - (xz,yz)] = 36,010$ cm.$^{-1}$. With the exception of $\Delta_2[(x^2 - y^2) - xy]$ these tetracoordinated one-electron molecular orbital parameters are similar to those uncovered previously for the octacoördinated cyanides (Fig. 6b). [Please keep in mind that here as throughout the text, the symbols s, x, y, z, xy, xz, yz, $x^2 - y^2$ and z^2 (and, at times, s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, $d_{x^2} - y^2$ and d_{z^2}—see Fig. 2b and 6a, b) do *not* imply that the molecular orbitals used are primarily ns, np or nd, ($n = 3, 4, 5$), in character. These symbols imply only that the molecular orbitals thereby specified have spatial charge amplitude distributions which angularly mimic those of the simple ns, np or nd distributions, but do *not*, in any sense, equal them. Of course in the simple linear combination of atomic orbital approximation these orbitals are pictured as composites of the metallic ns, np or nd functions and the ligand atomic functions; see Fig. 2a,c, 4, 5 and 10a, b]. The spectra of the Au·$(CN)_4^{-1}$, $Pd(CN)_4^{-2}$ and $Pt(CN)_4^{-2}$ anions were too diffuse to analyze and compare similarly.

(43) It is to be marked that our assignment neglects the possibility of a large Jahn–Teller separation for the ^1E_g or ^3E_g electronic state. Hence, some alteration in the theoretical parameterization would be required if this neglect were invalid. A discussion of the consequences of the Jahn–Teller theorem for systems with a single fourfold rotation or rotation-reflection axis [*e.g.*, C_{4v}, D_{3h}, D_{4d}, D_{2d}, etc., systems] may be found in (a) A. D. Liehr, "Progress in Inorganic Chemistry," Ed. F. A. Cotton, Interscience Publishers, Inc., New York N. Y., Vol. 4, 1962; (b) Annual Reviews of Physical Chemistry, Ed. H. Eyring, Annual Reviews, Inc., Palo Alto, Calif., Vol. 13, 1962, pp. 41–76 and in ref. 3f. [These discussions are based on the mathematical treatment given by (c) A. D. Liehr, *J. Phys. Chem.*, February, 1963]. Please keep in mind that the low symmetry of the octacyanide geometry (C_s) is *not* due to the Jahn–Teller theorem, but to ordinary coulombic and inelastic forces. For a discussion of the stereochemistry of such forces see ref. 43a,b and (d) A. D. Liehr, *J. Phys. Chem.*, February, 1963.

NOTE ADDED IN PROOF. Since this article went to press two further closely related works have appeared: (a) R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962) (on the octacyanides) and (b) B. R. McGarvey, *J. Chem. Phys.*, **37**, 2001 (1962) (on the perchromates). Golding and Carrington's octacyanide work is marred by a lack of spectral resolution and by a consequent theoretical misassignment. E. König (to be published) has corrected their treatment (Dr. König is presently a visiting Fellow at the Mellon Institute). Two additional related works which have appeared too late for inclusion in this paper are: H. L. Schläfer, E. König and H. von Hirschhausen, *Ann. chim.* (Rome), **52**, 663 (1962); and A. Bertoluzza and A. M. Marinangeu, *ibid.*, **52**, 667 (1962).

TABLE V

SPECTRAL DATA FOR THE d^8-TRANSITION METAL CYANIDE COMPLEX ANIONS

λ_{max}, mμ	ν_{max}, cm.$^{-1}$	ϵ_{max}	$f \times 10^{-4}$	Assignment	Calcd. frequency cm.$^{-1}$
			$Ni(CN)_4^-$		
		($F_2 = 11 F_4 = 770$ cm.$^{-1}$)			
266.0	37,590	16,150	965	Charge transfer	
284.0	35,220	4,820	310	Charge transfer	
309.5	32,300	770	71.5	$^1A_{1g} \rightarrow {}^1E_g$	Fitted
330.0	30,310	409	44.5	$^1A_{1g} \rightarrow {}^1A_{2g}$	Fitted
357.0	28,010	79	8.14	$^1A_{1g} \rightarrow {}^1B_{1g}$	Fitted
386.0	25,900	7.8	0.64	$^1A_{1g} \rightarrow {}^3A_{2g}$	25,410
426.0	23,470	~2.0	.24	$^1A_{1g} \rightarrow {}^3E_g$	24,880
486.0	20,580	~0.75	~.10	$^1A_{1g} \rightarrow {}^3B_{1g}$	19,750
		$Pd(CN)_4^-$: C. K. Jørgensen[40]			
212.0	47,800	9,000	...	Charge transfer	
220.5	45,400	7,200	(700)	Charge transfer	
240.2	41,600	1,200	54.0	Charge transfer	
		$Pt(CN)_4^-$: C. K. Jørgensen[40]			
242	(41,320)	1,850	200	Charge transfer	
255.2	39,180	29,500		Charge transfer	
258.4	(38,680)	26,000	3500	Charge transfer	
279.9	35,720	1,590	35.0	(?)	
		$Au(CN)_4^-$: A. Kiss, J. Csaszar and L. Lehotai[41a]			
217	46,083	2,400	...	Charge transfer	
264	37,879	331	...	(?)	
323	30,960	51	...	(?)	

= 3,4,5,6,7), the nitrosyls, the carbonyls, the mixed cyanides, nitrosyls and carbonyls, etc.]. In later publications we hope to report on whether this hope is justified or not. Our present progress within the d^n ($n = 3,4,5,6,7$), cyanide families is not sufficiently advanced at this time to give any indication of the true goodness of our theory. However, this circumstance should be rectified shortly, and we shall soon know how far elementary ligand field concepts can be pushed and still give valid results. When this latter question is answered, we shall have established once and for all the limits and boundaries of ligand field applications, and have set the frontiers for future experimental and theoretical advancement.