Volume 11
Number 3
March 1972

Inorganic Chemistry

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Intramolecular Environmental Effects on the Bonding in Transition Metal–Pentacyanonitrosyl Complexes

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Received June 3, 1971

The bonding characteristics of transition metal pentacyanonitrosyls are examined *via* molecular orbital calculations. Seven complexes of C_{4v} symmetry were studied. The results obtained are discussed in terms of orbital energetics and electronic distribution. Analysis of the data by statistical methods indicates that the square of the stretching frequencies of the nitrosyl groups can be correlated with the electron occupancy of the antibonding 2π orbital of the nitrosyl ligands. A notable exception to this is the results for $V(CN)_5NO^{5-}$ which further affirm the doubtful existence of this species. Correlation of the squares of the stretching frequencies of the in-plane cyanide ligands requires the orbital occupancies of both the 5σ and 2π orbitals of the cyanide groups. The results reinforce our contention that the nature of the total complex must be considered in the interpretation of trends between related species.

I. Introduction

In our recent studies on the bonding of cyanide and carbonyl ligands in metal complexes,[1] we observed that, in addition to variations in the electron occupancy of the 2π (antibonding) orbitals of the ligands, changes in the degree of σ donation of the "lone-pair electrons on the carbon atom" also occurred. Alteration of the σ-donating ability of the cyanide group was particularly noticeable. For example, on the basis of a Mulliken population analysis, each cyanide in $Mn(CN)_6^{5-}$ donated 0.69 electron to the metal whereas the cyanide group in $Mn(CO)_5CN$ transmitted 0.81 electron. We concluded that both the π-acceptor and σ-donor abilities of a ligand were dependent upon the nature of the other ligands present in the complex. Thus, cyanide is a better π acceptor and weaker σ donor in $Mn(CN)_6^{5-}$ than it is in $Mn(CO)_5CN$. Conversely, a carbonyl group is a much stronger π acceptor in $Mn(CN)_5CO^{4-}$ than in $Mn(CO)_6^+$ or $Mn(CO)_5CN$ but its σ-donor ability is only slightly altered.

The previous investigation was limited to isoelectronic systems of manganese complexes. The results obtained suggested that a study of a series of transition metal pentacyanonitrosyls could prove very fruitful. Data on seven such complexes of C_{4v} symmetry have been presented in the literature although the existence of one of them, $V(CN)_5NO^{5-}$, has been questioned.[2] The other six complexes are $V(CN)_5NO^{3-}$, $Cr(CN)_5NO^{3-}$, $Cr(CN)_5NO^{4-}$, $Mn(CN)_5NO^{2-}$, $Mn(CN)_5NO^{3-}$, and $Fe(CN)_5NO^{2-}$. If, for electron bookkeeping purposes, one considers the nitrosyl group as NO^+, the series involves metal d^4, d^5, and d^6 systems. Of particular interest are the ligand stretching frequencies which for the nitrosyl group vary from 1515 to 1929 cm^{-1}, while the cyanide stretches display a smaller range, 2020–2150 cm^{-1}. From a computational point of view, the series offers the challenge of anions of varying charges, metals, and d-orbital occupations, together with the availability of some structural and infrared experimental information. The generally accepted[3] contrast in π-acceptor ability of the nitrosyl and cyanide ligands coupled with the changes in the metal held out the promise of detecting variations in the σ-donor ability of the ligands. It is well known[4] that cyanide stretching frequencies can vary substantially in hexacyanide complexes. The relatively small range observed for the pentacyanonitrosyls suggested to us that alterations in the σ occupancies might be occurring.

II. Procedure

The computational methods used in this work are identical with those used previously.[1] For convenience, since the calculations are rotationally invariant, the nitrosyl ligand was presumed to be located along the positive z axis and the cyanides were presumed to be along the other axes of the coordinate system centered on the transition metal atom.

Of the seven complexes considered at the time this study was carried out, accurate X-ray data were known for $Na_2Fe(CN)_5NO \cdot 2H_2O$[5] and $K_3Mn(CN)_5NO \cdot 2H_2O$.[6]

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[1] R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971). For computational details see R. F. Fenske and R. L. DeKock, *ibid.*, **9**, 1053 (1970); K. G. Caulton and R. F. Fenske, *ibid.*, **7**, 1273 (1968); R. F. Fenske and D. D. Radtke, *ibid.*, **7**, 429 (1968); R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeny, *ibid.*, **5**, 951 (1966).

[2] S. Jagner and N. G. Vannerberg, *Acta Chem. Scand.*, **22**, 3330 (1968).

[3] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, pp 745–755.

[4] B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 82 (1966).

[5] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

[6] A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, **21**, 1462 (1967).

Available information on $K_3Cr(CN)_5NO$ yielded only limited information because of the disordered structure in the crystal.[7] Some preliminary data[2] were also available for $V(CN)_5NO^{3-}$. Consequently it was necessary to assign certain bond distances on the basis of reasonable, albeit somewhat arbitrary, choices. The final selections, based on the considerations to follow, are summarized in Table I. The table illustrates one of the decisions made, namely, that two complexes of the same metal with differing charges on the complexes were assigned the same atomic distances.

TABLE I

BOND DISTANCES (Å)

Complex	M–N	M–C	N–O	C–N
$Fe(CN)_5NO^{2-}$	1.63	1.90	1.13	1.16
$Mn(CN)_5NO^{2-,3-}$	1.66	1.98	1.21	1.16
$Cr(CN)_5NO^{3-,4-}$	1.66	2.04	1.21	1.16
$V(CN)_5NO^{3-,5-}$	1.66	2.18	1.21	1.16

The various distances for the iron and manganese complexes were based on the structural data of the two complexes cited above. These two structures also guided our selection of certain distances for the chromium and vanadium species. For example, both structures had the same carbon to nitrogen (cyanide) distance, 1.16 Å, and this value was used in all the complexes. Analogously, the metal to nitrosyl nitrogen in the two complexes differ by only 0.03 Å, so the larger of the two, 1.66 Å, was chosen for the corresponding distance in the other complexes.

Within a given complex all five metal to cyanide distances were set at the same value. For the iron and manganese complexes the structural data fixed these at 1.90 and 1.98 Å, respectively. Vannerberg's[7] examination of $K_3Cr(CN)_5NO$ showed it to have a disordered structure with an average metal to ligand distance of approximately 1.98 Å. With a metal to nitrosyl distance set at 1.66 Å, Vannerberg's work suggested a chromium to cyanide distance of about 2.04 Å since such a distance will result in the weighted mean value she obtained. For the vanadium complexes, the preliminary data by Jagner and Vannerberg[2] suggest 2.18 Å as the vanadium to cyanide distance.

The most difficult selection arose when we considered the nitrogen to oxygen distance of the nitrosyl group. Potentially this distance could be quite sensitive to the degree of back-bonding from the metal. However, without clear-cut experimental evidence to guide us and with the desire to examine changes in electron distributions primarily as a function of the nature of the metal and the number of d electrons involved in the system, we decided to fix the N–O distance at 1.21 Å, the value for the $Mn(CN)_5NO^{3-}$ species, for the chromium and vanadium complexes as well. For the iron complex, the N–O distance was set at the experimental value[5] found in $Na_2Fe(CN)_5NO \cdot 2H_2O$.

The basis functions chosen for the calculations of the overlap and approximate Fock matrices are linear combinations of Slater-type atomic orbitals. For the metal 1s to 3d orbitals, Richardson's[8] functions for the 1+ oxidation state were used. The metal 4s and 4p functions were generated by the method previously described.[9] The ligand atom basis functions were constructed from those of Clementi.[10,11] The basis functions correspond to those of the zero oxidation state for all ligand atoms except the nitrogen atom of the cyanide ligand for which the 1− functions were employed in keeping with the charge on the atoms as determined from the Mulliken population analysis. A complete set of all functions, eigenvalues, and eigenvectors has been filed with the ASIS National Auxiliary Publication Service.[12]

III. The Isolated Ligands

While the calculations were carried out using an atomic basis set, it will be useful to discuss the results in terms of changes within the ligand molecular orbitals. Our program permits reexpression of all matrices and eigenvectors in either set of basis functions. In order to make comparisons between the isolated and bonded ligands, calculations on the free ligands were carried out under the same approximations and distances used for the complexes. The resultant eigenvectors, eigenvalues, and overlap populations are given in Table II.

TABLE II

EIGENVECTORS, ORBITAL ENERGIES, AND OVERLAP POPULATIONS FOR THE FREE LIGANDS

CN^- Ligand

	$2S^C$	$2p^C$	$2S^N$	$2p^N$	*E*, eV	Overlap population
3σ	0.3499	−0.2111	0.6364	0.1293	−25.808	0.822
4σ	−0.4438	−0.2036	0.4560	−0.6341	−9.134	0.303
5σ	−0.5527	−0.7537	−0.2372	0.5898	3.057	−0.555
1π		0.4850		0.6927	−8.213	1.140
2π		−0.9921		0.8600	15.903	0.000

NO^+ Ligand at 1.13 Å

	$2S^N$	$2p^N$	$2S^O$	$2p^O$	*E*, eV	Overlap population
3σ	0.3787	−0.2378	0.6207	0.1638	−59.873	0.776
4σ	−0.4997	−0.2005	0.5201	−0.5954	−41.349	0.170
5σ	−0.5523	−0.6832	−0.2409	0.5321	−32.099	−0.226
1π		0.5337		0.7050	−37.048	0.873
2π		−0.8983		0.7712	−16.399	0.000

NO^+ at 1.21 Å

	$2S^N$	$2p^N$	$2S^O$	$2p^O$	*E*, eV	Overlap population
3σ	0.3810	−0.2353	0.6427	0.1573	−57.887	0.723
4σ	−0.5324	−0.1887	0.5249	−0.5730	−40.966	0.154
5σ	−0.5447	−0.6703	−0.2379	0.5332	−32.098	−0.174
1π		0.5390		0.7167	−35.743	0.783
2π		−0.8821		0.7449	−18.744	0.000

Since the 1s atomic orbitals were placed on core in the calculations, the molecular orbital labeling begins with

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(7) N. G. Vannerberg, *Acta Chem. Scand.*, **20**, 1571 (1966). After completion of these studies the crystal structure of $[Co(C_2H_8N_2)_3][Cr(CN)_5NO] \cdot 2H_2O$ was reported by J. H. Enemark, *et al.*, *Inorg. Chem.*, **9**, 2397 (1970). The internuclear distances were sufficiently similar to our estimates that a recalculation was not felt to be necessary. In fact, the NO distance in this ion is reported to be 1.21 Å which agrees with our estimate.

(8) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(9) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

(10) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

(11) E. Clementi in "Tables of Atomic Functions," a supplement to E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

(12) Materials supplementary to this article including all overlap matrices, eigenvectors, and eigenvalues have been deposited as Document No. NAPS-01613 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

3σ. Since CN^- and NO^+ are isoelectronic, the MO energy level ordering and occupations are the same: $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. Because of their importance in bonding within the complexes, the eigenvalues of the unoccupied 2π orbitals are also presented.

The differences in the eigenvalues of CN^- and NO^+ reflect the changes which occur on addition of a proton to each of the nuclei of CN^- to form NO^+. Each of the NO^+ energy levels are substantially stabilized relative to their CN^- counterparts. As shall be seen, analogous stabilization is maintained in the complexes and is important in the interpretation of the changes which occur in the electronic distributions among the series of molecules.

As we noted in our previous work,[1] the 5σ energy level, while primarily localized on the less electronegative atom, the carbon in CN^- and the nitrogen in NO^+, is an *antibonding* orbital with respect to σ bonding between the two atoms. Removal of electron density from this orbital will strengthen the σ bond. Correspondingly, occupation of the 2π orbitals *via* interaction with filled metal 3d orbitals will weaken the π bonding within the ligands.

IV. Results and Discussion

Energy Levels.—A characteristic feature of molecular orbital calculations on isolated anions or cations is that the absolute values of the resultant energy levels will reflect the overall charge on the species. Thus, as illustrated in the previous section, the negative charge on CN^- results in the placement of the occupied 5σ level at +3.057 eV. In the actual physical situation, this and the other levels of CN^- are stabilized by the cations and/or solvent dipole surrounding the species. The assumption in calculations of this sort is that the surroundings act as a spherically symmetric potential which is not explicitly included but which lowers all the diagonal terms in the Fock matrix and the final molecular energy levels by $q(27.2\text{ eV})/R$, where q is the effective charge and R is the distance in atomic units of that charge from the center of the system. In the species that are under consideration here, the anion charges range from 2− to 5− and hence their uncorrected eigenvalues differ substantially. We are primarily interested in their relative rather than absolute values so that scaling of the results to some standard is useful. Several approaches are possible. One could assume that the value of R for all the complexes is essentially constant and that the q values are the charges on the anions. Another possibility is to standardize all the energy levels to a single nonbonding orbital which is presumed to be essentially unaffected by complex formation. For example, one of the linear combinations of the π-bonding orbitals of the four planar cyanides is of A_2 symmetry and does not interact with any of the metal orbitals. All the energy levels could be scaled such that this molecular orbital has the same value in all the complexes. Each of these approaches has its merits and its limitations. In this report we have decided to employ a combination of the two. We have stabilized the eigenvalues of $Fe(CN)_5NO^{2-}$ by 7 eV. This value was selected by consideration of the charge on the complex, 2−, and the known internuclear distances. The metal to cyanide nitrogen distance is 5.78 au. Arbitrary addition of another 2.00 au to this distance to obtain an estimate of R yields a spherical potential of approximately 7 eV. Stabilization of the A_2 level in $Fe(CN)_5NO^{2-}$ by 7 eV places it at −17.24 eV. Then the eigenvalues in the complexes were scaled such that the A_2 level of each had this same value.

It might be noted that the scale factor required to obtain identical A_2 levels is approximately 4.5 eV per charge unit which suggests that $Fe(CN)_5NO^{2-}$ should be stabilized by 9 eV, but this would require an R value of about 6 au which is somewhat too small.

The scaled eigenvalues of the uppermost occupied levels are presented diagramatically relative to each other and the appropriate diagonal terms in the Fock matrices in Figure 1. No claim is made for the absolute accuracy of the eigenvalues obtained in this way. However, we do assert that relative trends, particularly when substantial changes are observed, are meaningful and give insight into the electronic structures of these species. Of course, this scaling only affects the relative energy of one complex compared to another, but it does not affect the separation of energy levels within a single species nor does it have any effect on the calculated charge distribution of the complexes.

Figure 1 illustrates that all of the complexes have several features in common. First of all, the levels of the nitrosyl group are substantially lower than their cyanide counterparts. However, the magnitudes of the separations are not nearly as large as exist in the isolated ions. For example, the 5σ level in free NO^+ is approximately 35 eV lower than the 5σ of free CN^- but in the complexes their separation does not exceed 15 eV and is frequently less than that. This alteration reflects the loss of electron density of the CN^- group and accumulation of electron density of the NO^+ group upon complex formation.

Notice that in all cases the NO^+ 5σ is well removed from and the CN^- 5σ is in close proximity to the metal 3d starting levels with the possible exception of $V(CN)_5NO^{5-}$. Simple perturbation theory suggests two consequences. First, the σ donation of a cyanide group should be greater than that of the nitrosyl group. Second, variations in the metal 3d levels should result in substantial fluctuations in the degree of σ donation by the cyanides but cause only minor changes in that of the nitrosyl group. This will be discussed in more detail in a later section.

The converse holds true for the 2π orbital interactions. That of the nitrosyl group should be stronger than that of the cyanide and be more susceptible to the nature of the metal atom and the number of "d electrons" in the system. The strong π interaction of the NO^+ group causes a splitting of the π-bonding "d orbitals of the metal" such that the 8e is more stable than the $2b_2$ molecular orbital. Such a result is in keeping with the traditional view of the stronger π-acceptor ability of NO^+ relative to CN^-.

The isoelectronic sequence from $Fe(CN)_5NO^{2-}$ through $V(CN)_5NO^{5-}$, diagrams a–d in Figure 1, displays the effects of successive removal of a proton from the metal nucleus. In $Fe(CN)_5NO^{2-}$, the 3d level is about 5 eV below that of the 2π NO^+ and approximately the same as that of the 5σ CN^-. Proton removal results in destabilization of the metal levels until, in the case of $V(CN)_5NO^{5-}$, the 3d is above the 2π

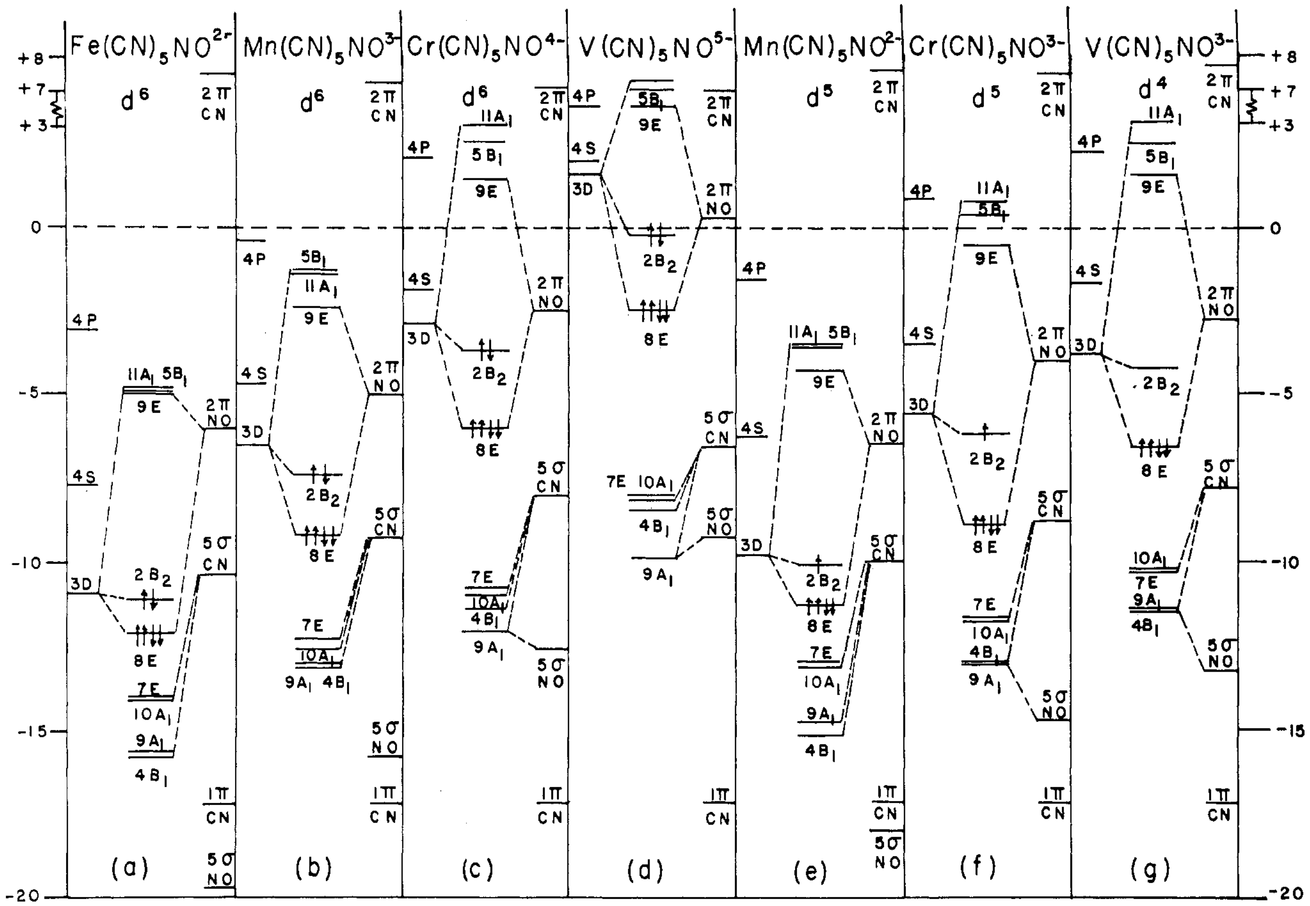

Figure 1.—Relative energy levels of the metal–pentacyanonitrosyl complexes $Fe(CN)_5NO^{2-}$, $Mn(CN)_5NO^{2-}$, $Mn(CN)_5NO^{3-}$, $Cr(CN)_5NO^{3-}$, $Cr(CN)_5NO^{4-}$, $V(CN)_5NO^{3-}$, and $V(CN)_5NO^{5-}$. Energy scale factors: (a) −7.00 eV, (b) −11.46 eV, (c) −6.50 eV, (d) −16.11 eV, (e) −20.37 eV, (f) −11.15 eV, (g) −10.61 eV.

NO^+ and far above the 5σ CN^-. Obviously this portends stronger 2π NO^+ participation and decreasing 5σ CN^- interaction through the sequence.

It is interesting to note that in the aforementioned series the filled molecular orbitals are also destabilized. Indeed, the value for the $2b_2$ orbital of $V(CN)_5NO^{5-}$ is so close to zero that minor adjustments in the approximations previously outlined for the placement of these energy levels could predict a value above zero for this species which, if correct, would lead to the conclusion that it could not exist. There is too much uncertainty in the calculational method and the use of the spherical potential unambiguously to make such a conclusion. Certainly one can say that the species would be highly susceptible to oxidation, particularly in the light of the known[13] reactivity of its isoelectronic chromium counterpart, $Cr(CN)_5NO^{4-}$. Further attention to the existence of $V(CN)_5NO^{5-}$ will be given later in this paper.

Because the levels in Figure 1 have been adjusted for the charges on the anions, diagrams e and b or f and c illustrate the destabilization of the molecular orbitals toward absolute zero as a consequence of electron addition. Furthermore, in both examples one is going from a d^5 to a d^6 configuration by adding an electron to the $2b_2$ molecular orbital. Even though this orbital involves bonding between the metal 3d orbitals and the π orbitals of the equatorial cyanides, the changes in the relative positions of the 3d levels with respect to the 2π NO^+ levels lead one to expect an increase of 2π NO^+ participation in the filled 8e molecular orbitals.

Since proton addition results in orbital stabilization and electron addition in destabilization, the simultaneous addition of a proton to the metal nucleus and an electron to the "metal 3d" orbital cannot be qualitatively predicted. The calculations suggest, diagrams b, f, and g of Figure 1, that for this series of complexes the overall effect is to stabilize the molecular orbitals. Of course, "stability" in the sense used here relates essentially to experiments such as photoelectron spectroscopy which can be correlated with particular molecular orbital energy levels and not to thermodynamic properties such as chemical reactivity. Specifically, the ionization of an electron from the filled 8e molecular orbital should require increasing energy through the series $V(CN)_5NO^{3-}$, $Cr(CN)_5NO^{3-}$, and $Mn(CN)_5NO^{3-}$. While it should not be expected that absolute ionization potentials can be predicted from these energy level diagrams with any high accuracy, it is felt that interpretation of any future results on the photoelectron spectra of these complexes can be aided by the diagrams of Figure 1.

Infrared Stretching Frequencies and Orbital Occupancies.—Of the complexes included in this study only $Fe(CN)_5NO^{2-}$ has thus far been the subject of an extensive force constant analysis.[13] However, some infrared data are available for each of the complexes. In particular, a few of the bands associated

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[13] W. P. Griffith, *J. Chem. Soc.*, 3286 (1963).

TABLE III

INFRARED STRETCHING FREQUENCIES (CM^{-1})

Complex	ν_{NO}	ν_{CN}	Ref
$Fe(CN)_5NO^{2-}$	1935	2170, 2160 2158, 2142^a 2125, 2109 2098	*b*
$Mn(CN)_5NO^{2-}$	1885	2150,^{a} 2100	*c*
$Mn(CN)_5NO^{3-}$	1725	2130, 2101^a 2060	*b*
$Cr(CN)_5NO^{3-}$	1630	2120,^{a} 2073	*b*
$Cr(CN)_5NO^{4-}$	1515	2020^a	*d*
$V(CN)_5NO^{3-}$	1530	2110^a	*e*
$V(CN)_5NO^{5-}$	1575	. . .	*f*

[a] The most intense band in the set, chosen as the e vibrational mode. See text. [b] P. Gans, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, **5,** 1877 (1966). [c] F. A. Cotton, R. R. Monchamp, R. J. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10,** 28 (1959). [d] W. P. Griffith, *J. Chem. Soc.*, 3286 (1963). [e] S. Jagner and N. G. Vannerberg, *Acta Chem. Scand.*, **22,** 3330 (1968). [f] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1632 (1959).

with the cyanide and nitrosyl stretches have been identified. These are summarized in Table III. It is apparent from the paucity of information that force constants, even within the Cotton–Kraihanzel[14] approximation, are not feasible. Nevertheless within the limits of certain assumptions, meaningful information and insights are possible.

In C_{4v} symmetry, the five cyanide stretches are basis functions for 2 A_1 + B_1 + E irreducible representations and the nitrosyl stretch belongs to the A_1 representation. Of these, the A_1 and E normal modes are infrared active. As illustrated by Abel and Butler,[15] the most intense mode of the cyanide groups should be associated with the E irreducible representation. As shown by Cotton and Kraihanzel[14] the relation between the stretching frequency, ν, and the force constant, k, can be approximated for the E representation by $5.889 \times 10^{-2}\nu^2 = \mu(k - k_t)$, where μ is the reciprocal of the reduced mass of the CN^- group and k_t is the interaction constant between pairs of trans cyanide groups. If one assumes that for the series of complexes under consideration the values of k_t are constant, then the relative changes in CN^- stretching frequencies of the most intense cyanide band should reasonably reflect the relationships between the CN^- force constants.

Since the nitrosyl group and two of the cyanide modes are bases for the A_1 irreducible representation, one should solve a 3 × 3 determinant with appropriate values of k_{NO}, k_{CN^-}, and various k_c and k_t interaction constants in order to go from the nitrosyl stretch to the NO force constant. However, since there are insufficient data available for such an analysis and the changes in NO stretching frequencies are of such appreciable magnitude, we will assume, as a first approximation, that the relation between the force constant and the frequency is that of the diagonal term in the secular determinant, *i.e.*, $5.889 \times 10^{-2}\nu_{NO}^2 = \mu_{NO}k_{NO}$.

The foregoing paragraphs suggest that if the results of our molecular orbital calculations for the ground-state geometries can be correlated with the force constants between the atoms, then we should observe a correlation between our results and the squares of the frequencies.

The generally accepted explanation of trends in force constants and hence changes in stretching frequencies of ligands such as carbonyl, cyanide, and nitrosyl on bonding to transition metals lies in the π-acceptor ability of the ligands.[16] However, the importance of changes in the degree of σ donation is gaining recognition.[17] Our previous work suggested that whether one or both effects will be operable depends upon the total molecular environment. The present study sheds additional light on this concept.

As in our previous work,[1] we have chosen to analyze the electronic distributions within the complexes in terms of the Mulliken population analysis. On doing so, we found that for both the cyanide and nitrosyl ligands the electronic structures of the 3σ, 4σ, and 1π orbitals were unchanged from those of the free ions. Only the 5σ and 2π orbital occupancies appear to be affected by complex formation. These orbital occupations and those of the metal orbitals are presented in Table IV.

TABLE IV

ORBITAL OCCUPATIONS OF $M(CN)_5NO^{n-}$ COMPLEXES

		M							$Mn(CN)_6^{5-}$
		Fe	Mn	Cr	V	Mn	Cr	V	
		n							
		2	3	4	5	2	3	3	5
		d							
		d^6	d^6	d^6	d^6	d^5	d^5	d^4	d^6
1 CN	5σ	1.19	1.22	1.31	1.43	1.22	1.29	1.35	1.31
	$2\pi_x$	0.06	0.08	0.11	0.15	0.04	0.05	0.01	0.14
	$2\pi_y$	0.05	0.06	0.07	0.06	0.05	0.05	0.04	0.14
6 CN	5σ	1.20	1.27	1.34	1.46	1.23	1.30	1.36	1.31
	$2\pi_x$	0.05	0.06	0.07	0.06	0.05	0.05	0.04	0.14
	$2\pi_y$	0.05	0.06	0.07	0.06	0.05	0.05	0.04	0.14
5 NO	5σ	1.51	1.52	1.52	1.53	1.52	1.52	1.53	. . .
	$2\pi_x$	0.56	0.78	0.94	1.10	0.66	0.83	0.90	. . .
	$2\pi_y$	0.56	0.78	0.94	1.10	0.66	0.83	0.90	. . .
Metal	d_{z^2}	0.90	0.78	0.68	0.60	0.89	0.77	0.76	0.68
	$d_{x^2-y^2}$	1.00	0.86	0.73	0.57	0.98	0.83	0.76	0.68
	d_{xz}	1.44	1.14	0.91	0.75	1.34	1.09	1.03	1.51
	d_{yz}	1.44	1.14	0.91	0.75	1.34	1.09	1.03	1.51
	d_{xy}	1.84	1.76	1.59	1.42	0.95	0.87	0.01	1.51
	d total	6.62	5.68	4.82	4.09	5.50	4.65	3.59	5.89
	4s	0.54	0.50	0.44	0.32	0.53	0.48	0.42	0.48
	$4p_x$	0.58	0.55	0.52	0.44	0.56	0.54	0.49	0.56
	$4p_y$	0.58	0.55	0.52	0.44	0.56	0.54	0.49	0.56
	$4p_z$	0.54	0.52	0.49	0.41	0.53	0.51	0.47	0.56
Metal total		8.86	7.80	6.79	5.70	7.68	6.72	5.46	8.06

The electronic distributions presented in Table IV reinforce the conclusions suggested by the energy level diagrams, namely, in the case of the cyanide ligands notable changes occur in the occupancies of both the 5σ and 2π orbitals while for the nitrosyl group the 2π occupancies change but those of the 5σ are essentially constant. To obtain more quantitative measures of these conclusions, we carried out a statistical analysis of the linear correlation between ν^2 of the E mode stretching frequencies and the 5σ and 2π occupancies of the equatorial cyanide ligands, since it is the latter that are involved in the E vibration. Similarly, a statistical analysis of the ν^2 for the nitrosyl stretches *vs.* the 5σ and 2π nitrosyl occupations was completed. For reasons to be seen, the linear relation of the nitrosyl ν^2 values with only the 2π occupancy was also studied. The results are summarized in Table V.

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(14) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84,** 4324 (1962).

(15) E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, **63,** 45 (1967).

(16) Reference 3, p 731.

(17) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7,** 959 (1968).

TABLE V

CORRELATION OF SQUARED FREQUENCIES WITH ORBITAL OCCUPATIONS[a]

Equatorial Cyanides

Equation: $\nu^2 \times 10^{-6} = 7.401 - 3.306(2\pi) - 2.054(5\sigma)$

Std error of estimate 47 cm^{-2}

Variable	Coeff	Partial correlation	*t* value	Partial *F* value	Significance, %
Constant	7.401	0.995	16.63	276.4	99.9
π coeff	−3.306	−0.972	−7.16	51.2	99.4
σ coeff	−2.054	−0.960	−5.93	35.2	99.0

Nitrosyl—σ and π

Equation: $\nu^2 \times 10^{-6} = 1.467 - 2.155(2\pi) + 3.156(5\sigma)$

Std error of estimate 117 cm^{-2}

Variable	Coeff	Partial correlation	*t* value	Partial *F* value	Significance, %
Constant	1.467	0.078	0.14	0.02	10.0
π coeff	−2.155	−0.985	−9.75	95.05	99.8
σ coeff	3.156	+0.244	0.44	0.19	30.3

Nitrosyl—π Only

Equation: $\nu^2 \times 10^{-6} = 6.175 - 2.102(2\pi)$

Std error of estimate 104.3 cm^{-2}

Variable	Coeff	Partial correlation	*t* value	Partial *F* value	Significance, %
Constant	6.175	0.997	23.94	573.4	100.0
π coeff	−2.102	−0.998	−12.84	164.9	99.9

[a] The correlations were determined with values of the orbital occupations carried out to one more significant figure than those reported in Table IV. The exact values are contained in the documents filed with the ASIS.[12]

The results given in Table V are most gratifying and informative. In the case of the cyanide ligands the mutual importance of the 5σ and 2π occupations is reflected in the similar magnitude of their regression coefficients, their partial correlation coefficients, and the significance levels of the statistical "*t*" and "*F*" tests. There is no question that the final stretching frequency of the cyanide group depends upon the balance between 5σ donation, which strengthens the C to N bond, and the 2π acceptance, which weakens the C to N bond.

The data on the nitrosyl group are equally illuminating. When both the 5σ and the 2π occupations are included, the statistics reject the contribution of the 5σ occupancies as aiding the correlations. Furthermore, the coefficient is of opposite sign compared to what one must expect from the antibonding character of this orbital. An examination of the actual occupancies of the nitrosyl 5σ orbitals in Table IV clearly indicates that they are essentially constant for the series of complexes. This is in keeping with the large energy separation of the nitrosyl 5σ from the metal d levels. The statistical data on the correlation of ν^2 with the 2π occupations gives further emphasis to this conclusion. The uncertainty in the constant term in the linear equation disappears, and the standard error of estimate is improved. Obviously, it is only the back-bonding to the nitrosyl 2π that is responsible for the trend in the stretching frequencies through the series.

The results obtained in this work emphasize that the importance of σ donation on the bond strengths within ligand groups depends not only on orbital availability, in the sense of using good overlap as a criterion, but also upon orbital *energetics*. Thus, the cyanide stretching frequencies were dependent upon the 5σ occupations while the nitrosyl stretching frequencies were not because the cyanide orbitals were of such energy as to result in substantial fluctuations in the degree of interaction with the metal 3d orbitals. On the other hand, the nitrosyl levels were sufficiently removed that alteration in the metal 3d levels did not cause substantial variation in the character of their bonding wave functions. These conclusions reinforce the contention of our earlier work that the description of bonding interactions frequently requires that the total molecular environment be considered. It should be emphasized that the independence of the trend in nitrosyl stretching frequencies to the nitrosyl 5σ occupancy is not necessarily general. For example, in complexes such as $Mn(CO)(NO)_3$ and $Fe(CO)_2(NO)_2$, the nitrosyl groups constitute a substantial portion of the ligand environment, and alterations in the 5σ might possibly occur.

The Existence of $V(CN)_5NO^{5-}$.—It should be noted that the previous statistical analysis does not include the results on $V(CN)_5NO^{5-}$. The doubtful existence[2] of this complex has already been mentioned and the possibility that the highest filled molecular orbitals would be above zero in energy has also been discussed. If one accepts the correlation of stretching frequencies of the nitrosyl groups with the 2π occupations, the infrared data concerning this species become suspect. Figure 2 is a diagram of the linear relation between ν^2 of the nitrosyl group and the 2π orbital occupancy obtained from the statistical analysis. It is very clear from the figure that if our assumptions are correct, the complex in question would have a nitrosyl stretching frequency of the order of 1250 cm^{-1} rather than the reported value of 1575 cm^{-1}. Needless to say, there was much head scratching about our results concern-

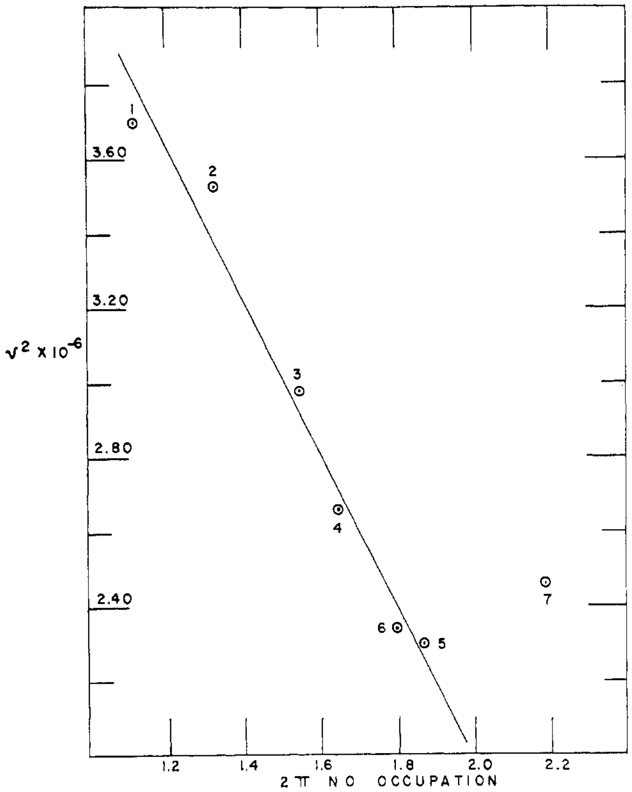

Figure 2.—Correlation of ν_{NO}^2 with 2π NO occupations.

ing this species until ref 2 was discovered. Since the completion of these calculations, a private communication from Masek[18] suggests that the actual species obtained by the preparative method is a mixed polyvanadate. It is gratifying that the calculations indicated something was amiss, for one of the purposes that approximate calculations must be capable of serving is not only to obtain correlations with experimental observables but also not to obtain correlations when they do not exist. To do so requires a method which minimizes the possibility of unconscious incorporation of the researcher's preconceptions of what the answer should be.

Bonding in the Complexes.—The interplay of cyanide σ donation and π acceptance, of nitrosyl π acceptance, and of the nature of the metal reinforces our earlier contention[1] that the total intramolecular environment must be considered in dealing with trends among related complexes. The data in Table IV can be used to illustrate the features of the relationships.

The complexes $Cr(CN)_5NO^{4-}$, $Fe(CN)_5NO^{2-}$, $Mn(CN)_5NO^{3-}$, and $Mn(CN)_6^{5-}$ are isoelectronic, differing only in the number and placement of additional protons. The data on the hexacyanide complex were obtained from our previous work and are included in Table III for comparative purposes. Conceptually, one can relate $Mn(CN)_6^{5-}$ to $Mn(CN)_5NO^{3-}$ *via* the addition of a proton to the carbon and nitrogen nuclei of one cyanide group converting it from CN^- to NO^+. The entire molecular species readjusts to the electron-drawing power of these protons. The nitrosyl group retains substantially more 5σ electron density than do the cyanides and its π-acceptor ability is phenomenally larger. This, of course, is to be expected. What is intriguing is that most of the electron flow to the nitrosyl is at the expense of the cyanide ligands and not the metal atom. The metal d_{xz} and d_{yz} orbitals each lose 0.37 electron on going from $Mn(CN)_6^{5-}$ to $Mn(CN)_5NO^{3-}$, but there is substantial compensation by increased occupancy of both the π-bonding d_{xy} and the σ-bonding d_{z^2} and $d_{x^2-y^2}$ orbitals so that the overall loss by the metal is only 0.21 electron. The five cyanides lose electrons from the 5σ and 2π orbitals, both of which are antibonding in character. Thus, the observed cyanide stretching frequency increase, from 1930 cm^{-1} for $Mn(CN)_6^{5-}$ to 2101 cm^{-1} for $Mn(CN)_5NO^{3-}$, reflects an increase in both σ- and π-bond strength.

While alteration of the nature of the ligands by proton addition to the ligand nuclei did not drastically change the total 3d occupancy, an analogous conceptual process to change the metal from chromium to manganese to iron does affect the 3d populations. All five of the 3d orbitals increase in electron occupation along this series and they do so by drawing electron density from all six ligands. The nitrosyl group alone transfers approximately 0.30 electron for each proton added to the metal nucleus and, as previously indicated, this transfer is from the 2π nitrosyl orbitals. However, the loss of electron density from the cyanides again involves both the 5σ and 2π orbitals.

A particularly informative set of comparisons is to examine the occupations of complexes carrying the same overall charge, *e.g.*, $Mn(CN)_5NO^{3-}$, $Cr(CN)_5NO^{3-}$, and $V(CN)_5NO^{3-}$. We can relate these three species by envisioning the simultaneous loss of a proton from the metal nucleus and an electron from the filled $2b_2$ orbital. This latter orbital involves the interaction of the metal d_{xy} and the cyanide $2\pi_x$ orbitals in the XY plane. For the cyanides, two effects are simultaneously taking place. There is a loss in the 2π occupation which would result in a strengthening of the carbon-nitrogen bond. However, there is an increase in 5σ population with a resultant weakening of the carbon-nitrogen bond. The two effects essentially counterbalance one another so that the differences in the stretching frequencies, Table III, are negligible. This same counterbalancing was previously suggested as a qualitative explanation of the constancy of the stretching frequencies in the series $M(CN)_6^{3-}$ with M = Cr, Mn, Fe, and Co.[19]

The increase in cyanide 5σ populations mentioned in the previous paragraph is a consequence of the destabilization of the metal 3d levels as indicated by Figure 1. There is a decrease in the metal orbital participation and an increase in the 5σ cyanide orbital participation in the resultant σ molecular orbitals. Consequently, there is an increase in the 5σ occupation. This same 3d level destabilization results in an increase in the interaction of the metal $3d\pi$ orbitals with the 2π orbitals of the nitrosyl group. An increased amount of electron density is transferred to the 2π nitrosyl orbitals which results in the observed decrease in nitrosyl stretching frequencies for the series. An analogous relationship holds for the two complexes carrying a 2− charge, $Fe(CN)_5NO^{2-}$ and $Mn(CN)_5NO^{2-}$.

Further insight can be obtained by comparison of d^5 and d^6 systems involving the same metal, such as $Mn(CN)_5NO^{2-}$ and $Mn(CN)_5NO^{3-}$ or $Cr(CN)_5NO^{3-}$ and $Cr(CN)_5NO^{4-}$. In each case, the sixth electron is added to the $2b_2$ molecular orbital. Since this orbital involves the π interaction of the planar cyanide groups with the metal, a reduction in the cyanide stretching frequencies is to be expected. That this reduction is not greater than what is actually observed is explained by the increased 2π occupation of the nitrosyl group. Thus, even though the electron was added to an orbital not directly involved with the nitrosyl, substantial alteration of electron density within this group occurs because of electron redistribution throughout the entire molecular system. Notice that although the $2b_2$ orbital is primarily metal in character and indeed its orbital occupancy does increase on addition of the sixth electron, the total 3d occupancy undergoes only slight alteration. The similarity of total 3d orbital occupations in, *e.g.*, $Mn(CN)_5NO^{2-}$ and $Mn(CN)_5NO^{3-}$, emphasizes that formal oxidation states are simply useful devices for purposes of electron bookkeeping and do not reflect actual electron density distributions.

It is worthwhile noting that the trends in ligand electron density were all interpreted relative to CN^- and NO^+ even though the final densities of the ligands in the complexes may be different. These choices are a matter of conceptual convenience since the two ligands in this form are isoelectronic and "closed shell," *i.e.*, with 5σ orbitals occupied and 2π orbitals virtual. To infer

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[18] J. Masek, private communication; *Inorg. Chim. Acta*, in press.

[19] L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

that the nitrosyl group in $Mn(CN)_5NO^{3-}$ is like a neutral NO molecule because its total density is nearly the same is very misleading if not erroneous. The neutral NO group has a fully occupied 5σ orbital and a single *unpaired* electron in the 2π orbitals. The nitrosyl group in the complex has less than two electrons in the 5σ orbital and the 2π density it possesses consists of *paired* electrons contributed to it by virtue of participation in the filled molecular orbitals of E representation. While it is frequently convenient to relate groups of atoms in a complex to their free ligand counterparts, we should not lose sight of the fact that such devices are primarily for conceptual utility.

Acknowledgment.—The authors wish to thank the National Science Foundation (Grant GP-6057) and the Wisconsin Alumni Research Foundation for support of this work.

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Kinetic and Equilibrium Studies of *cis*-Bis(oxalato)isothiocyanatoaquochromate(III)

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Received March 29, 1971

The acidity constant of *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ has been determined spectrophotometrically at 1.0 ± 0.5° and $\mu = 2.0$ *F* ($NaNO_3$) to be $(8.7 \pm 3.0) \times 10^{-8}$ *F*. The formation quotient for *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ at $\mu = 1.00$ *F* ($NaNO_3$) has been determined at 25, 35, 45, and 55° to be 4.50 ± 0.06, 5.25 ± 0.12, 5.53 ± 0.07, and 5.60 ± 0.04 F^{-1}, respectively. The values of $\Delta H°$ and $\Delta S°$ were determined to be 1.2 ± 0.4 kcal/mol and 7.3 ± 1.4 cal/deg mol, respectively. The kinetics of aquation of *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ were pH independent from pH 3 to pH 4 and at $\mu = 1.00$ *F* ($NaNO_3$). The overall aquation reaction occurred with retention of configuration. The values of k_1 at 25, 35, 45, and 55° were $(1.61 \pm 0.11) \times 10^{-5}$, $(4.98 \pm 0.11) \times 10^{-5}$, $(1.59 \pm 0.01) \times 10^{-4}$, and $(4.09 \pm 0.01) \times 10^{-4}$ sec^{-1}, respectively. The values of ΔH^* and ΔS^* were 20.1 ± 0.4 kcal/mol and −13.1 ± 1.2 cal/deg mol. The aquation reaction was concluded tentatively to occur by an I_d mechanism.

Introduction

There have been very few reports of compounds of the type *cis*-$Cr(C_2O_4)_2XY^{n-}$, where X and Y are simple monodentate ligands.[1] There have been even fewer reports of kinetic and equilbrium studies. Recently the synthesis of the ion *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ has been reported.[2] In order to understand more about the equilibrium and kinetic properties of the *cis*-$Cr(C_2O_4)_2^{-}$ moiety, the aquation of *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ was studied. The formation quotient of the ion was determined, and the acidity constant of the *cis*-$Cr(C_2O_4)_2NCS(OH_2)^{2-}$ was determined. This paper reports the results of these studies.

Experimental Section

All chemicals used were reagent grade and were used without further purification. The sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.[3] Solutions of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) were prepared and analyzed as previously reported.[2]

The spectra of solutions of chromatographically separated pure sodium *cis*-bis(oxalato)diaquochromate(III) at pH 3 in 0.10 *F* sodium nitrate and of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) at pH 3 in 2.0 *F* sodium nitrate were determined at 2° using a Beckman DU-2 spectrophotometer with a 0.10-mm slit width. The spectrum of *cis*-bis(oxalato)isothiocyanatohydroxochromate(III) was determined at 1° and at pH 9.0 in a solution of sodium hydroxide and 2.0 *F* sodium nitrate using a Cary Model 15.

The experiment designed to attempt to separate the possible cis and trans isomers of $Cr(C_2O_4)_2NCS(OH_2)^{2-}$ was essentially identical with the ones previously reported for the partially successful separation of *cis*- and *trans*-$Cr(C_3H_2O_4)_2(OH_2)_2^{-}$.[4] However, 2.0 *F* $NaNO_3$ at pH 3 was used as eluent and ten fractions containing Cr(III) were collected.

The rate studies were performed using a Beckman DU-2 fitted with a specially constructed constant-temperature block which completely surrounded the 10-cm cell used and a Cary Model 15 fitted with the commercially available constant-temperature block. The temperature was maintained to within ±0.1° of that desired. The rate of aquation was followed at 412 and 550 nm, the wavelengths of maximum absorbance change, using an approximately 0.40 m*F* solution of sodium *cis*-bis(oxalato)diaquochromate(III) as the reference solution. To prepare the solutions for the kinetic runs, the following procedure was used. A solution of about 2.0 m*F* sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) in 2.0 *F* sodium nitrate at 0° and pH 2.0–3.0 was mixed with the appropriate amount of water at pH 2.0–3.0 and at an elevated temperature so that the final solution had an ionic strength of 1.0 *F* and had the desired temperature. The solution was poured immediately into a 10-cm cuvette, the cuvette was placed into the constant-temperature block, and the change in absorbance with time was monitored. The change in absorbance in various runs was from 0.20 to 0.50.

The formation quotients of sodium *cis*-bis(oxalato)isothiocyanatoaquochromate(III) were determined by ion-exchange chromatography. Five-milliliter aliquots containing 0.10 *F* sodium *cis*-bis(oxalato)diaquochromate(III) (previously purified by anion-exchange chromatography), various amounts of sodium thiocyanate from 0.100 to 0.900 *F*, and enough sodium nitrate to maintain the ionic strength at 1.00 *F* were sealed in glass ampoules and thermostated at the desired temperature, 25–55°. The solutions were allowed to react for various time intervals from seven to nineteen days to ensure that equilibrium had been attained. After the desired time, the ampoules were opened and the solutions run into Dowex 1-X8, 200–400 mesh, nitrate-form anion-exchange columns maintained at 1°. A flow rate of 3.0 ml hr^{-1} was used. The columns were washed with 0.10 *F* sodium nitrate to ensure elution of sodium *cis*-bis(oxalato)-

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(1) Gmelin, "Gmelin's Handbuch der anorganischen Chemie," 8 Auflage, Chrom Teil C, Verlag Chemie, Weinheim, Germany, 1965, reported the synthesis of ions in which X = Y for X = NH_3 (p 234), X = C_2H_7N (p 274), X = C_6H_7N (p 280), X = C_5H_5N (p 289), and X = $C_{19}H_{20}N_2O$ (cinchonin) (p 289).

(2) S. Kulprathipanja and K. R. Ashley, *J. Inorg. Nucl. Chem.*, **32**, 3965 (1970).

(3) A. Werner, *Ann.*, **406**, 216 (1914).

(4) K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).