β_1^2/Δ, where $\Delta = E_{B_{2g}} - E_{B_{1g}}$. We do not know either β_1 or Δ with certainty. The optical transition observed in the visible region lies in the range expected for Δ, but we cannot assign it clearly to this transition because of its strong solvent dependence. It is likely that the relatively weak d–d transition is obliterated by a strong band. The value of β_1 probably lies between 0.8 and 1.0. If we admit that Δ is in the range between 17 and 25 kK, we obtain values for α between 0.71 and 0.84.

The ligand contribution α' to the ground state can be estimated from the normalization conditions; we may take for the overlap integral $\langle d_{x^2-y^2}| -\sigma_x\rangle = 0.17$ which is obtained considering the cyanide σ orbitals to be sp hybrids and taking the Cu–C distance to be 1.9 A, which is a weighted average of the metal–carbon distance for a number of complex cyanides of similar structure. This value gives for α' the limits $0.98 > \alpha' > 0.89$ for $0.71 < \alpha < 0.84$. The values of α' thus obtained are unusually high. They are quite reasonable, though, if we consider the great instability of the complex, which can thus be related to the large degree of delocalization of the "hole" in the d shell over the ligands.

If we use Kivelson's formula for α[19]

$$\alpha^2 = -\frac{A}{P} + (g_{\parallel} - 2) + \frac{3}{7}(g_{\perp} - 2) + 0.04$$

we obtain the value $\alpha = 0.78$, which lies midway between the limits found above.

7. Conclusions

The epr and optical spectra of the purple unstable species obtained adding CN^- to Cu^{II} solutions in various solvents at low temperature can be interpreted as belonging to the essentially square-planar complex, $[Cu(CN)_4]^{2-}$. All of the experimental facts are satisfactorily accounted for by this interpretation. In particular, the theoretical interpretation of the parameters of the spin Hamiltonian yield a degree of delocalization of the electron "hole" which is higher than those observed for most other Cu^{II} complexes, a fact which may be correlated with the great instability of the species under study.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The Electronic Spectra of Hexanitrometalates

BY KENNETH G. CAULTON[1] AND RICHARD F. FENSKE

Received September 9, 1966

The charge-transfer spectra of the hexanitro complexes of Co^{3+}, Rh^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} are reported. Contrary to a previous interpretation, an analysis of the solid-state infrared spectra of the various $Co(NO_2)_6^{3-}$ salts indicates that the principal deviation from T_h symmetry involves a rotation of the nitro groups about the Co–N axis. A molecular orbital energy level diagram which accounts for the charge-transfer spectra of the hexanitrometalates is presented. By means of this diagram the weak band at 21.5 kK in $Co(NO_2)_6^{3-}$ is shown to be an orbitally forbidden charge-transfer transition from a nonbonding oxygen orbital to the predominantly metal e_g orbital. Proper assignment of this transition obviates anomalous spectroscopic properties previously attributed to the nitro group.

Although the nitro group is taken as a classic example of a π-acceptor ligand[2] and the prevailing theory of the *trans* effect is based upon its back-bonding ability,[3] recent evidence from the Mössbauer effect[4] attributes equal π-bonding ability to NO_2^- and NH_3. Electronic spectra also provide evidence which is seemingly contradictory in nature. Since d-to-d spectra are blue shifted from $Co(NH_3)_6^{3+}$ to $Co(NH_3)_5NO_2^{2+}$, it has been concluded that the nitrite ion provides a stronger field than NH_3.[5] However, the first band of $Co(NH_3)_6^{3+}$ *red* shifts on passing to $Co(NO_2)_6^{3-}$.[6] This anomaly has been interpreted as indicating coordination through oxygen in $Co(NO_2)_6^{3-}$,[5] but the absence of a metal–oxygen stretching fundamental at 1050 cm^{-1} makes such an explanation highly doubtful. The red shift of the first band on going from $Rh(NH_3)_6^{3+}$ to $Rh(NO_2)_6^{3-}$ only serves to compound the confusion.[7]

Recently Krause, Wickenden, and Ruggles (KWR)[8] have shown, in agreement with others,[9] that the infrared spectra of $M_3Co(NO_2)_6$ are dependent upon the cation M^+. They claim that the visible spectra show a similar dependence. The spectra of the Na^+ and K^+ salts are interpreted by KWR as arising from an axial elongation along two Co–N bonds. However, KWR conclude the cesium salt, $Cs_3Co(NO_2)_6$, has all Co–N bond lengths equal and derive values of the ligand field

---

(1) Predoctoral National Science Foundation Fellow.

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 853.

(3) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1963).

(4) E. Flück, *Advan. Inorg. Chem. Radiochem.*, **6**, 433 (1964).

(5) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).

(6) A. Kiss and D. Czeglédy, *Z. Anorg. Allgem. Chem.*, **235**, 407 (1938).

(7) H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **47**, 96 (1964).

(8) R. Krause, A. Wickenden, and C. Ruggles, *Inorg. Chem.*, **5**, 936 (1966).

(9) I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *ibid.*, **3**, 772 (1964).

parameter Δ and the electronic interaction parameters B and C from its absorption spectrum in the solid state. The spectrum of the cesium salt reported by KWR differs markedly from that observed in solution. As a result of their spectral interpretation, KWR find it necessary to assign a value of 81 to the ratio C/B, compared to the usual value of 4 which holds for free ions and most complexes. In addition, the derived value of B is so small that the nephelauxetic[10] ratio, $\beta = B(\text{complex})/B(\text{free ion})$, is only 0.05. If true, such a β value is quite extraordinary since it would be the first example ever to fall outside the range 0.3–1.0.[11] As will be seen, a more reasonable explanation is possible.

In what follows, we shall attempt to resolve the anomaly of the Δ values for $M(NO_2)_6{}^{3-}$ ($M = Co^{3+}$, Rh^{3+}) and, in so doing, interpret the charge-transfer spectra of the di- and trivalent transition metal hexanitro complexes. For a satisfactory explanation it is mandatory to take account of the oxygen atoms which lower the anion symmetry from O_h to T_h. Although one still has the degeneracy of the t_{2g} and e_g sets as in O_h (thus the d $\rightarrow$ d spectra are unaffected), these atoms have a profound effect upon the charge-transfer and infrared spectra.

Experimental Section

Compounds were prepared according to published methods [12–14] and gave infrared spectra in agreement with those previously observed.[14] Only the compound of Fe^{2+} was sensitive to air and/or moisture, and this was prepared in an inert-atmosphere bag and stored in a vacuum desiccator over Drierite.

Infrared spectra were run from 2000 to 600 cm^{-1} on a Perkin-Elmer 421 spectrophotometer and from 600 to 400 cm^{-1} on a Beckman IR10 spectrophotometer in KBr pellets. Visible and ultraviolet spectra were scanned on a Cary 14M spectrophotometer. Electronic spectra were run as KCl pellets, mineral oil mulls, and, where possible, aqueous solutions. Potassium chloride prepared according to the method of Hales and Kynaston[15] gave completely transparent pellets when pressed at 250,000 psi in a vacuum die. It was found that evacuation of the die gave pellets with reduced scattering and that KCl was superior to KBr not only because it is less hygroscopic but also because it is transparent to 2000 A. The small amount of complex needed to observe the charge-transfer spectra clouded the pellets negligibly. Such is not the case for the d-to-d spectra, and therefore tissue paper moistened with mineral oil was placed between Suprasil plates and positioned flush against the detector side of the sample and reference pellets.[16] This technique gives a marked enhancement of absorbed light relative to that scattered. A typical spectrum is given in Figure 1. Because of substantial differences in absorption intensities, it was necessary to form four separate pellets of varying concentration in order to obtain the absorption maxima. Consequently, it is impossible to obtain relative intensities of the absorption maxima. However, as indicated by Figure 1, the intensities increased systematically with increasing frequency.

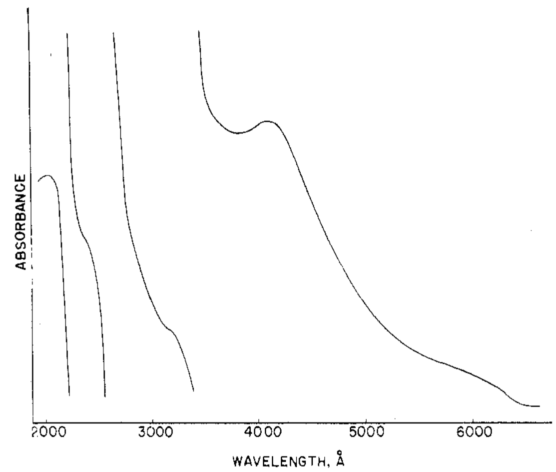

Figure 1.—Electron spectrum of $K_2BaFe(NO_2)_6$.

TABLE I

ELECTRONIC SPECTRA OF $M_3Co(NO_2)_6$

	ν, kK[a]				Medium
$Cs_3Co(NO_2)_6$		26.8	37.6	48.6	KCl
$K_3Co(NO_2)_6$		27.1	37.7	46.1	KCl
$Na_3Co(NO_2)_6$		26.0	37.8	47.9	KCl
$K_3Co(NO_2)_6$[b]	21.5	28.2	37.6	48.1	H_2O
	(235)	(5180)	(10,500)	(32,600)	

[a] 1 kK = 1000 cm^{-1}. [b] The molar absorptivity appears in parentheses.

Results

Table I presents maxima observed above 11 kK for $M_3Co(NO_2)_6$ with M = Na, K, Cs. No other structure was found except for asymmetry on the low-energy side of the 27-kK band due to the weak 21.5-kK shoulder which is also seen in solution. None of the bands seen by KWR in the 12–17-kK region is observed in this work. In addition, contrary to the results of KWR, the electronic spectra are found to be independent of the cation. The frequencies in Table I agree with the reflectance spectrum of $K_3Co(NO_2)_6$,[17] indicating our technique yields results comparable to reflectance spectroscopy.[18] Infrared studies show $Na_3Co(NO_2)_6$ is the most distorted of all $Co(NO_2)_6{}^{3-}$ species, yet the electronic spectrum of this salt mulled in mineral oil exhibits no bands in the region 12.5–18 kK. Finally, a 1.4 *M* aqueous solution of $Na_3Co(NO_2)_6$ in a 1-cm cell showed no structure in the region 12.5–16 kK.

Explaining the bands observed by KWR is not a trivial problem. It is known, however, that care must be exercised in preparing and interpreting solid-state spectra. Sharp bands observed in powdered samples of dimethylglyoxime complexes are absent in single-crystal spectra.[19] Reflectance spectra are known to yield spurious peaks if the sample is too concentrated or if environmental effects at the solid surface are important.[20,21] Artifacts may also appear as weak bands if the sample particles are too large.[22] Finally, one

---

[10] C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1963).

[11] (a) KWR attempt to make their value plausible with the claim that $Co(dtp)_3{}^{3+}$ is expected to have $\beta = 0.02$. (b) The spectrum of this species has been observed and it is found that $\beta = 0.36$: C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

[12] C. Przibylla, *Z. Anorg. Allgem. Chem.*, **15**, 419 (1897).

[13] P. Ray and H. Sahu, *J. Indian Chem. Soc.*, **23**, 161 (1946).

[14] H. Elliott, B. Hathaway, and R. Slade, *Inorg. Chem.*, **5**, 669 (1966).

[15] J. Hales and W. Kynaston, *Analyst*, **79**, 702 (1954).

[16] K. Shibata, A. Benson, and M. Calvin, *Biochem. Biophys. Acta*, **15**, 461 (1954).

[17] A. Babaeva and R. Rudyi, *Zh. Neorgan. Khim.*, **1**, 921 (1956).

[18] H. Zeitlin and A. Niimoto, *Nature*, **181**, 1616 (1958).

[19] G. Basu, G. Cook, and R. L. Belford, *Inorg. Chem.*, **3**, 1361 (1964).

[20] T. Griffiths, K. Lott, and M. Symons, *Anal. Chem.*, **31**, 1338 (1959).

[21] F. A. Cotton and M. D. Myers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

[22] G. Kortüm, *Spectrochim. Acta*, **11**, 534 (1956).

notes that KWR's prediction of four d-to-d transitions using three crystal field parameters does not necessarily prove their assignment correct; Liehr[23] has shown that it is possible to fit the spectrum of NiF_2 with d^3 energy matrices!

Discussion

Structure.—Before proceeding further, we must dispose of the problem of the actual structure of the hexanitro complexes. $K_2BaCo(NO_2)_6$,[24] $K_3Co(NO_2)_6$,[25] and $K_4Ni(NO_2)_6$[26] have all been shown to have nitrogen octahedra about the metal with the oxygens disposed to give T_h symmetry (Figure 2). As shown in Figure 3, rotation of all nitro groups by an *arbitrary* small angle lowers the symmetry to S_6, D_2, or T. A small angle is chosen since the distortion will be dictated by packing forces and not by any strong orientational force within the complex ion itself. The structure proposed by KWR belongs to point group D_{2h} when the oxygen atoms are included (Figure 3d). The number of infrared-active bands for various models appearing in Figure 3 is shown in Table II. The observation, by Nakagawa, *et al.*,[9] of three or more bands in the NO_2 antisymmetric stretching region of $Na_3Co(NO_2)_6$ eliminates the T and S_6 models. This is corroborated by KWR's observation of three Co–N stretching frequencies. The remaining D_{2h} and D_2 models can be distinguished in the NO_2 asymmetric stretching region. The observations of a cluster of at least five bands (Figure 4) eliminates the D_{2h} structure. The infrared spectrum of $Na_3Co(NO_2)_6$ is therefore compatible with the D_2 structure. Of course, lower symmetries resulting from a more random rotation of the nitro groups cannot be rigorously excluded.

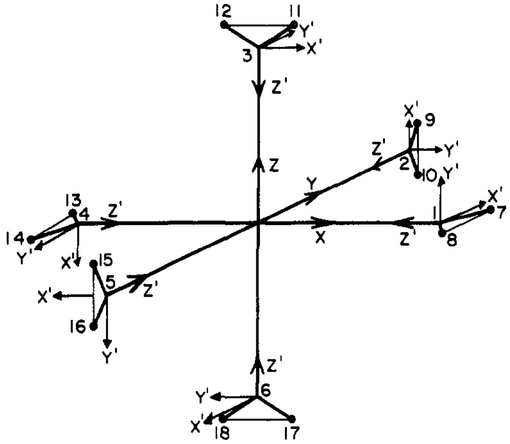

Figure 2.—Coordinate system for $M(NO_2)_6$ species of T_h symmetry. In terms of the central metal coordinates, atoms 7, 8, 13, and 14 lie in the *xy* plane, atoms 9, 10, 15, and 16 in the *yz* plane, and atoms 11, 12, 17, and 18 in the *xz* plane. All oxygen coordinate systems are right-handed with the positive region of the p_z orbital along the N–O bond. The positive region of the p_x oxygen orbital for atoms 7, 8, 13, and 14 points in the central metal *z* direction, atoms 9, 10, 15, and 16 point in the metal *x* direction, and atoms 11, 12, 17, and 18 point in the metal *y* direction.

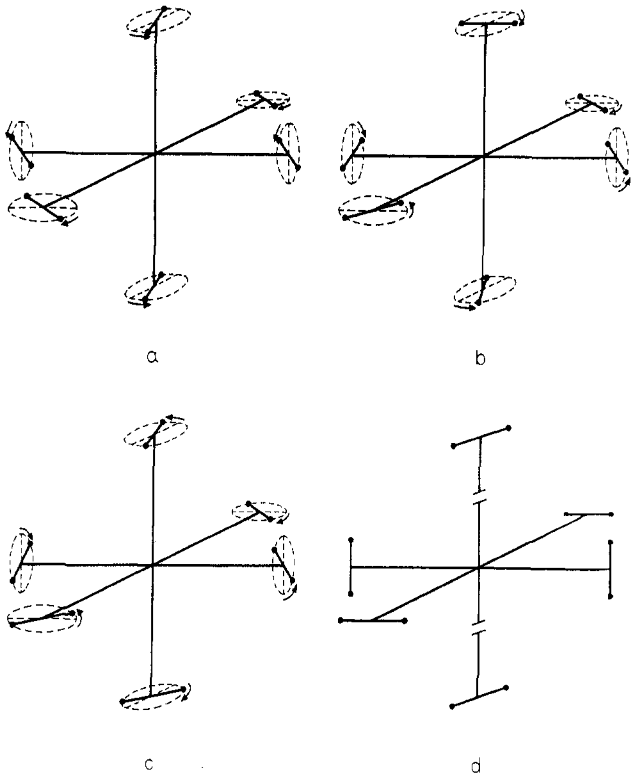

Figure 3.—Some distortions of $Co(NO_2)_6^{3-}$ from T_h symmetry: (a) S_6, (b) D_2, (c) T, (d) D_{2h}.

TABLE II

NUMBER OF INFRARED-ACTIVE VIBRATIONS OF $M(NO_2)_6$ FOR VARIOUS SYMMETRIES

Type of vibration	T_h	T	S_6	D_2	D_{2h}
NO_2 antisym str	1	2	2	6	3
NO_2 sym str	1	1	2	3	3
NO_2 bend	1	1	2	3	3
NO_2 wag	1	2	2	6	3
Co–N str	1	1	2	3	3
NO_2 rock	1	2	2	6	3
NO_2 twist	0	1	2	3	0
NCoN def	2	3	4	9	6

Lowering the symmetry of the anion by reorientation of the oxygen atoms rather than lengthening two Co–N distances is far more satisfactory theoretically. The ^1A_g state of $Co(NO_2)_6^{3-}$ is not subject to a Jahn–Teller distortion and the relatively weak crystal forces are more suited to a low-energy rotation of oxygens about the Co–N line than the energetically were costly lengthening of a Co–N bond. Several X-ray studies support this reasoning.[26,27] It is, therefore, clear that when a distortion of the $Co(NO_2)_6^{3-}$ species occurs, it involves only the oxygen atoms. While such a distortion from T_h symmetry may occur in some hexanitrometalates, it has no observable effect on the electronic spectra. The following analysis will therefore be based on T_h symmetry.

Laport-Forbidden Transitions.—It is our contention that, contrary to previous assumptions, the lowest energy transition observed in both $Co(NO_2)_6^{3-}$ and Rh-

---

[23] A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

[24] J. Bertrand and D. Carpenter, *Inorg. Chem.*, **5**, 514 (1966).

[25] M. van Driel and H. J. Verweel, *Z. Krist*, **A95**, 308 (1936).

[26] A. Ferrari, L. Calvaca, and M. Nardelli, *Gazz. Chim. Ital.*, **81**, 945 (1951); L. Calvaca, M. Nardelli, and D. Grazioli, *ibid.*, **86**, 1041 (1956).

[27] S. Simonsen and M. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 309 (1965).

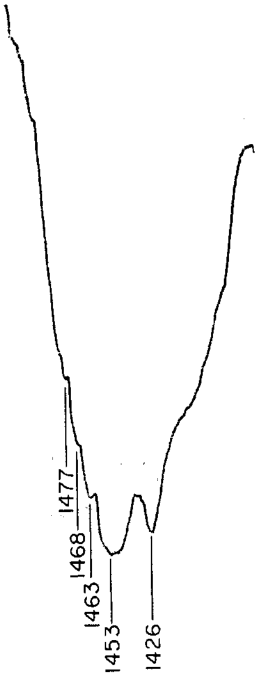

Figure 4.—NO_2 antisymmetric stretching band of $Na_3Co(NO_2)_6$. The shoulder on the low-energy side of this band (about 1390 cm^{-1}) is due to a NO_3^- impurity.

$(NO_2)_6^{3-}$ is *not* a ligand field transition. There are several reasons for this.

If one assigns the lowest energy transition as $^1A_g \rightarrow {}^1T_g$, then it is reasonable to expect that the $^1A_g \rightarrow {}^3T_g$ transition should be observed at an energy $2C$ lower. Using a β value for NO_2^- interpolated between NH_3 and CN^- and taking $C = 4B$, one calculates that the spin-forbidden band should appear at approximately 4 kK for Co and 3 kK for Rh below the $^1A_g \rightarrow {}^1T_g$ transition. Guided by the spin-forbidden intensities observed in cyanide, ammine, chloride, and oxalate complexes of Co^{3+} and Rh^{3+},[28-30] molar absorptivities of 0.3 and 3 are expected for the $^1A_g \rightarrow {}^3T_g$ bands of $Co(NO_2)_6^{3-}$ and $Rh(NO_2)_6^{3-}$, respectively. As stated above, no band of this description is observed in a 1.4 *M* aqueous solution of $Na_3Co(NO_2)_6$, the same being true for a saturated (~1 *M*) aqueous solution of $Na_3Rh(NO_2)_6$ in a 1-cm cell.

Furthermore, the appreciable intensity of the lowest energy transition of $Rh(NO_2)_6^{3-}$[7] makes a d-to-d assignment quite doubtful. The intensity ratio $\epsilon(RhL_6)/\epsilon(CoL_6)$ for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition has never been found to exceed 3; taking $\epsilon[Co(NO_2)_6^{3-}] = 235$, one expects a molar absorptivity for $Rh(NO_2)_6^{3-}$ of less than 700 in contrast to the observed 2380.

A preferable prediction as to the location of the ligand field transitions of these trivalent hexanitro complexes is facilitated by Jørgensen's empirical factorization of Δ and β into a product of ligand and metal factors.[31] Application of this procedure to the well-characterized $Ni(NO_2)_6^{4-}$ spectrum[14] indicates that the nitro group has 1.18 times the ligand field strength of ethylenediamine (en). Use of this ratio on Co^{3+} yields a Δ value of 27.4 kK for $Co(NO_2)_6^{3-}$. Similarly, from the data of Elliott, *et al.*,[14] $\beta = 0.72$ for $Ni(NO_2)_6^{4-}$. Since the ratio $\beta(CoL_6)/\beta(NiL_6)$ for L = H_2O, NH_3, and en has an average value of 0.66, β for $Co(NO_2)_6^{3-}$ can be estimated as $(0.66)(0.72) = 0.48$. Hence, from B(complex) = βB(free ion), one obtains B(complex) = 0.53 kK. In the strong-field approximation $^1A_g \rightarrow {}^1T_g$ should appear at $\Delta - C = \Delta - 4B = 25.3$ kK where it would be masked by charge-transfer transitions (Table I).

Similarly, the ratios $\Delta(RhL_6)/\Delta(CoL_6)$ for L = H_2O, $C_2O_4^{2-}$, NH_3, and ethylenediamine cluster closely about the value 1.48, thus yielding $\Delta[Rh(NO_2)_6^{3-}] \approx 40.6$ kK. For the same series of ligands $\beta(Rh)/\beta(Co) \approx 1.13$ so one predicts $\beta[Rh(NO_2)_6^{3-}] \approx 1.13(0.48) = 0.54$ and $B = 0.4$ kK. With these parameters, the first spin-allowed transition would appear at 39 kK where it would again be masked by charge-transfer bands.

It is possible to validate the Δ value predicted for $Co(NO_2)_6^{3-}$ and also obtain some insight into the anomalous red shift of the first band from $Co(NH_3)_6^{3+}$ to $Co(NO_2)_6^{3-}$ by examination of the first bands of the intermediate species $Co(NH_3)_{6-x}(NO_2)_x^{3-x}$ which are summarized in Table III. The rule of average environment[31] allows the calculation of a band position for MA_xB_{6-x} from the frequencies of the related peaks in MA_6 and MB_6

$$\nu(MA_xB_{6-x}) = \frac{x}{6}\nu(MA_6) + \frac{6-x}{6}\nu(MB_6)$$

The results of such a calculation appear in Table III; ν has been taken to be 25.3 kK for the hexanitro complex and 21.2 kK for the hexaammine. The agreement for the mono-, di-, and trinitro complexes makes it clear that the Δ and B values proposed here for $Co(NO_2)_6^{3-}$ are very likely correct. The red shift from $Co(NH_3)_2(NO_2)_4^-$ to $Co(NH_3)(NO_2)_5^{2-}$ shows that it is not only the hexanitro complex which is "anomalous." Instead, a gradual reversal of the expected trend occurs. Such a phenomenon could result from the simultaneous blue shift of a d-to-d band and a red shift of a weak charge-transfer band, the latter finally appearing completely resolved in $Co(NO_2)_6^{3-}$. Further evidence in support of this hypothesis will be presented later.

TABLE III

SPECTRA OF $Co(NH_3)_{6-x}(NO_2)_x^{(3-x)+}$

Species	ν (calcd), kK	ν (obsd), kK	Ref
$Co(NH_3)_6^{3+}$	...	21.2	*a*
$Co(NH_3)_5NO_2^{2+}$	21.9	21.75	*a*
trans-$Co(NH_3)_4(NO_2)_2^+$	22.6	22.6	*a*
$Co(NH_3)_3(NO_2)_3$	23.2	23.1	*a*
$Co(NH_3)_2(NO_2)_4^-$	23.9	23.4	*a*
$CoNH_3(NO_2)_5^{2-}$	24.6	22	*b*
$Co(NO_2)_6^{3-}$	...	21.5	*a*

[a] Reference 6. [b] M. Shibata, M. Mori, and E. Kyuno, *Inorg Chem.*, **3**, 1573 (1964).

Charge-Transfer Transitions.—Table IV contains

---

[28] M. Mingardi and G. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).

[29] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1502 (1954).

[30] C. K. Jørgensen, *ibid.*, **10**, 500 (1956).

[31] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., Oxford, 1962.

TABLE IV

SYMMETRY-ADAPTED LIGAND FUNCTIONS FOR $M(NO_2)_6$ SPECIES[a]

Irreducible repn (T_h)	Ligand function[b]
A_g	$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$
	$\pi_{1y}^- + \pi_{2y}^- + \pi_{3y}^- - \pi_{4y}^- - \pi_{5y}^- - \pi_{6y}^-$
A_u	$\pi_{1x}^- + \pi_{2x}^- + \pi_{3x}^- - \pi_{4x}^- - \pi_{5x}^- - \pi_{6x}^-$
E_g	$[2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5, \sigma_1 - \sigma_2 + \sigma_4 - \sigma_5]$
	$[2\pi_{3y}^- - 2\pi_{6y}^- - \pi_{1y}^- - \pi_{2y}^- + \pi_{4y}^- + \pi_{5y}^-, \pi_{1y}^- - \pi_{2y}^- - \pi_{4y}^- + \pi_{5y}^-]$
E_u	$[2\ \pi_{3x}^- - 2\ \pi_{6x}^- - \pi_{1x}^- - \pi_{2x}^- + \pi_{4x}^- + \pi_{5x}^-, \pi_{1x}^- - \pi_{2x}^- - \pi_{4x}^- + \pi_{5x}^-]$
T_g	$[x_1' + x_5' + y_2' + y_4', x_3' + x_4' + y_1' + y_6', x_2' + x_6' + y_3' + y_5']$
	$[x_1' + y_4' - y_2' - x_5', x_3' + y_6' - x_4' - y_1', x_2' + y_5 - x_6' - y_3']$
	$[m_1 - m_4, m_3 - m_6, m_2 - m_5]$
	$[\pi_{1y}^+ + \pi_{4y}^+, \pi_{3y}^+ + \pi_{6y}^+, \pi_{2y}^+ + \pi_{5y}^+]$
	$[\pi_{2x}^+ - \pi_{5x}^+, \pi_{1x}^+ - \pi_{4x}^+, \pi_{3x}^+ - \pi_{6x}^+]$
	$[\pi_{3x}^- + \pi_{6x}^-, \pi_{2x}^- + \pi_{5x}^-, \pi_{1x}^- + \pi_{4x}^-]$
T_u	$[x_3' + y_2' - x_5 - y_6', x_1' + y_3' - y_4 - x_6', x_2' + y_1' - y_5' - x_4']$
	$[x_3' + x_5' - y_2' - y_6', x_1' + x_6' - y_3' - y_4', x_2' + x_4' - y_1' - y_5']$
	$[\sigma_1 - \sigma_4, \sigma_2 - \sigma_5, \sigma_3 - \sigma_6]$
	$[m_3 + m_6, m_1 + m_4, m_2 + m_5]$
	$[\pi_{2x}^+ + \pi_{5x}^+, \pi_{3x}^+ + \pi_{6x}^+, \pi_{1x}^+ + \pi_{4x}^+]$
	$[\pi_{1y}^- + \pi_{4y}^-, \pi_{2y}^- + \pi_{5y}^-, \pi_{3y}^- + \pi_{6y}^-]$
	$[\pi_{3y}^+ - \pi_{6y}^+, \pi_{1y}^+ - \pi_{4y}^+, \pi_{2y}^+ - \pi_{5y}^+]$

[a] As in Figure 5, primed coordinates refer to N, unprimed to O. The atoms are numbered as in Figure 2. [b] $\sigma_n = S_n', Z_n', {}^1/_2(q_{2n+5} + q_{2n+6})$ with $q = S, Z$ and $n = 1$–6. $m_n = {}^1/_2(q_{2n+5} - q_{2n+6})$ with $q = S, Z$ and $n = 1$–6. $\pi_{nq}^\pm = {}^1/_2(q_{2n+5} \pm q_{2n+6})$ with $q = x, y$ and $n = 1$–6.

those linear combinations of atomic orbitals which transform according to the irreducible representations of T_h. The order of the energy levels of the free nitrite ion has been established on the basis of Pariser–Paar–Pople calculations on NO_2^-,[32] spectra of NO_2^-,[33] ionization potentials for NO_2,[34] and extended Hückel calculations on NF_2.[35] With these facts in hand, an energy level diagram for $M(NO_2)_6$ species of T_h symmetry can be constructed by relating the symmetry-adapted atomic orbitals to the known molecular orbitals (MO) of the free nitrite ion (Table V and Figure 5). The resulting diagram (Figure 6) exhibits many features common to an energy level diagram for a complex of O_h symmetry. In particular, the potential back-bonding ability of the nitro group arises from mixing of the t_g ligand level (derived from the π-antibonding b_1^* orbital of NO_2^-) with the metal 3d t_g orbital. One significant difference from O_h symmetry should be noted, however. A nonbonding π orbital of NO_2^- participates in molecular orbitals of symmetry a_u and e_u. Since the metal valence orbitals do not contain this representation, these orbitals are totally nonbonding; this will be of importance in what follows.

The spectra of the first transition series hexanitro complexes and $Rh(NO_2)_6^{3-}$ are given in Table VI, but

TABLE V

MOLECULAR ORBITALS OF THE NITRITE ION[a]

$$b_1^* = 0.78X' - \frac{0.63}{\sqrt{2}}(X_1 + X_2)$$

$$a_1^* = \frac{0.83}{\sqrt{2}}(Y_1 - Y_2) - \frac{0.34}{\sqrt{2}}(Z_1 + Z_2) + 0.38Z' + 0.25S'$$

$$b_2 = \frac{-0.99}{\sqrt{2}}(Y_1 + Y_2) + \frac{0.15}{\sqrt{2}}(Z_1 - Z_2)$$

$$a_2 = \frac{1}{\sqrt{2}}(X_1 - X_2)$$

$$b_1 = 0.63X' + \frac{0.78}{\sqrt{2}}(X_1 + X_2)$$

$$a_1 = \frac{0.54}{\sqrt{2}}(Y_1 - Y_2) + \frac{0.24}{\sqrt{2}}(Z_1 + Z_2) - 0.74Z' - 0.33S'$$

[a] See ref 32. The coordinate system is that shown in Figure 5.

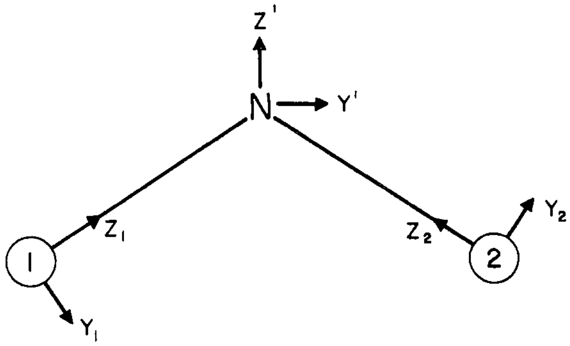

Figure 5.—Coordinate system for the nitrite ion. All atoms lie in the plane of the paper, with the p_x orbitals (X', X_1, and X_2) coming out of the page toward the reader. The nitrogen and oxygen 2s orbitals are denoted S′ and S, respectively.

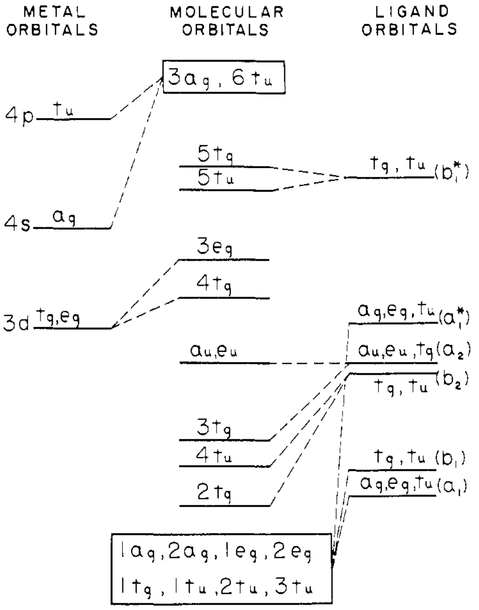

Figure 6.—Energy level diagram for $M(NO_2)_6$ species of T_h symmetry. A dotted line connects each molecular orbital to that symmetry orbital which dominates the linear combination of atomic orbitals. To the right of the T_h irreducible representation of the ligand function appears the C_{2v} symmetry label of the participating free NO_2^- molecular orbital (see Table V).

---

(32) K. L. McEwen, *J. Chem. Phys.*, **34**, 547 (1961).
(33) S. Strickler and M. Kasha, *J. Am. Chem. Soc.*, **85**, 2899 (1963).
(34) Y. Tanaka and A. Jursa, *J. Chem. Phys.*, **36**, 2493 (1962).
(35) J. J. Kaufman, private communication.

TABLE VI

CHARGE-TRANSFER SPECTRA OF HEXANITROMETALATES[a]

Sample	ν, kK	Assignment
$Cs_3Co(NO_2)_6$	21.5[b]	$(a_u, e_u) \rightarrow e_g$
	26.8	$^1A_g \rightarrow {}^1T_u(1a)$
	37.6	$\rightarrow {}^1T_u(1b), {}^1T_u(2a)$
	48.6	$\rightarrow {}^1T_u(2b)$
$Na_3Rh(NO_2)_6$	31.5	$^1A_g \rightarrow {}^1T_u(1a)$
	36.4	$\rightarrow {}^1T_u(1b)$
	>50	$\rightarrow {}^1T_u(2a)$
$K_2BaFe(NO_2)_6$[c]	20.0[f]	$(a_u, e_u) \rightarrow e_g$
	24.4	$^1A_g \rightarrow {}^1T_u(1a)$
	31.0	$\rightarrow {}^1T_u(1b)$
	40.8	$\rightarrow {}^1T_u(2a)$
	50.0	$\rightarrow {}^1T_u(2b)$
$K_2BaCo(NO_2)_6$[d]	23.0	$(a_u, e_u) \rightarrow e_g$
	28.4	$^2E_g \rightarrow {}^2T_u(1a)$
	34.4	$\rightarrow {}^2T_u(1b)$
	39.9	$\rightarrow {}^2T_u(2a)$
	49.5	$\rightarrow {}^2T_u(2b)$
$K_2CaNi(NO_2)_6$[e]	28.6	$^3A_g \rightarrow {}^3T_u(1a)$
	33.0	$\rightarrow {}^3T_u(1b)$
	40.2[f]	$\rightarrow {}^3T_u(2a)$
	48.5	$\rightarrow {}^3T_u(2b)$
$K_2CaCu(NO_2)_6$	22.1	$(a_u, e_u) \rightarrow e_g$
	27.0[g]	
	38.3[g]	
	49.7[g]	

[a] All spectra in KCl pellets excepted as noted. [b] Very weak shoulder in KCl pellet. Frequency quoted is that of $Na_3Co(NO_2)_6$ in solution. [c] $K_4Fe(NO_2)_6$ displayed a similar spectrum. [d] The salts $K_4Co(NO_2)_6$, $K_2CaCo(NO_2)_6$, and $K_2PbCo(NO_2)_6$ all displayed the bands quoted here. [e] $K_4Ni(NO_2)_6$ showed similar bands. [f] Very weak shoulder. [g] Not assigned under T_h symmetry due to tetragonal distortion. See ref 14.

the likelihood of Jahn–Teller distortions[14] in $Cu(NO_2)_6{}^{4-}$ dictates that it not be considered in the following analysis.

The near identity of the frequency of the first transition in $NO_2{}^-$ with that of the intense transition in $Co(NO_2)_6{}^{3-}$ at 27 kK has led to the assignment of the latter as an intraligand $n \rightarrow \pi^*$ transition.[6,7] This is difficult to accept for two reasons. First, the $a_1{}^*$ nonbonding orbital from which the free-ion transition originates[33] is σ bonding[32] with the metal and therefore the MO's derived from it will be stabilized considerably (Figure 6). Thus, the $n \rightarrow \pi^*$ transition should exhibit a substantial blue shift in the species $M(NO_2)_6$. Second, although formally allowed, the free-ion $n \rightarrow \pi^*$ transition is very weak. It can gain intensity only by strong mixing with metal orbitals, with a concomitant shift in frequency. Thus, the negligible frequency shift coupled with a 300-fold increase in intensity is incompatible with an $n \rightarrow \pi^*$ intraligand assignment. A similar argument shows that the intraligand $\pi \rightarrow \pi^*$ transition should blue shift from its free-ion value of about 50 kK.

It is significant that the first two intense bands exhibit a striking similarity in trends along the d^6 isoelectronic series. The relation $\nu(Co^{3+}) > \nu(Fe^{2+})$ establishes these as metal-to-ligand charge-transfer transitions. In point group T_h the dipole operator transforms as T_u, so only transitions to T_u states are allowed from an A_g ground state. The metal-to-ligand excitation $4t_g \rightarrow 5t_u$ is unusual since it gives rise to *two* T_u states; assignment of the first two intense bands as transitions to these two states accounts for the above observations. This pair of states, $T_u(1a)$ and $T_u(1b)$, corresponds to the T_{1u} and T_{2u} states which arise from a $t_{2g} \rightarrow t_{1u}$ excitation in O_h symmetry.[36] In the O_h case however, the transition to the T_{2u} state is forbidden; since the octahedral MN_6 framework carries over into $M(NO_2)_6$, the nitrogen symmetry adapted functions remain unchanged from their form in O_h (see Table IV) and all intensity to $T_u(1b)$ in T_h arises from integrals involving oxygen orbitals. The terms $T_u(1a)$ and $T_u(1b)$ are split in energy by an amount[37]

$$2\{(t_u(y)t_g(xy)|t_g(xz)t_u(z)) - (t_u(y)t_u(z)|t_u(xz)t_g(xy))\}$$

by virtue of electrostatic interaction. An examination of these integrals shows that one-center Coulomb integrals over nitrogen orbitals (usually about 15 ev) will dominate. When this value is multiplied by the square of the coefficient of the nitrogen p_π orbital in the $4t_g$ orbital (0.3–0.4 for hexachloro complexes[38]), a value comparable to the observed 1-ev splitting is obtained. Additional support for the proposed assignment comes from vibrational structure seen in the analogous band (25.7 kK) of $K_2CaCu(NO_2)_6$ in CH_3CN. Four peaks are clearly resolved with a spacing of 10^3 cm^{-1}. Sidman[39] observes progressions of 1013 cm^{-1} in the $n(a_1{}^*) \rightarrow \pi^*(b_1{}^*)$ band of solid $NaNO_2$ which he assigns to the symmetric stretching mode of $NO_2{}^-$. This vibrational frequency is lower than the ground-state value (1345 cm^{-1} [40]) since the electronic excitation $n \rightarrow \pi^*$ weakens the N–O bond. For $M(NO_2)_6$ species, the electronic transition $A_g \rightarrow T_u$ can couple with α_g, ϵ_g, and τ_g vibrations, but only the first two contain a symmetric stretching motion of the nitro groups. Further, only single quantum progressions in the α_g mode will have appreciable intensity.[41] It follows that the α_g frequency which may appear in the $A_g \rightarrow T_u$ band will be lowered from its value in the ground electronic state if the $4t_g \rightarrow 5t_u$ electronic assignment is correct since the $5t_u$ MO involved is composed primarily of the $\pi^*(b_1{}^*)$ orbital involved in the $NO_2{}^-$ transition; population of the N–O antibonding $5t_u$ MO thus weakens the N–O bond just as it did in the free ion.

The third and fourth intense bands are logically considered as a pair by virtue of their similar trends with the changing central metal. (The 37.5-kK band of $Co(NO_2)_6{}^{3-}$ is presumably composed of two transitions.) These bands are characteristic[42] of ligand to metal transitions since $\nu(Fe^{2+}) > \nu(Co^{3+})$. The lowest energy transition of this type is $4t_u \rightarrow 3e_g$ which again gives rise to two T_u states, $T_u(2a)$ and $T_u(2b)$, in accord with the observed spectra. Relating the T_h orbitals to those of O_h, the $4t_u \rightarrow 3e_g$ transition corresponds to $t_{2u} \rightarrow e_g$ which yields states T_{1u} and T_{2u},

---

(36) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

(37) For notation see R. Fenske, K. Caulton, D. Radtke, and C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

(38) D. Radtke and R. Fenske, to be published.

(39) J. Sidman, *J. Am. Chem. Soc.*, **79**, 2669 (1957).

(40) R. Weston and T. Brodasky, *J. Chem. Phys.*, **27**, 683 (1957).

(41) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 76 (1941).

(42) C. K. Jørgensen, *Mol. Phys.*, **2**, 309 (1959).

only the former being allowed in O_h. A situation similar to that discussed above therefore obtains; two transitions are predicted and observed where only one would appear if the anion symmetry were idealized to O_h.

The charge-transfer spectra of $Co(NO_2)_6^{4-}$ and $Ni(NO_2)_6^{4-}$ in the region 28–50 kK are very similar to the spectra of the d^6 species. As in the d^4 cases, the excitations $4t_g \rightarrow 5t_u$ and $4t_u \rightarrow 3e_g$ each give rise to pairs of states of symmetry T_u. It therefore seems appropriate to assign the four observed bands as transitions to these allowed states. However, for these d^7 and d^8 species, the transition $3e_g \rightarrow 5t_u$ is also allowed and is expected to appear at an energy Δ less than that of the $4t_g \rightarrow 5t_u$ transition. Since Δ for these species is in the range 13.5–16.5 kK,[14,43] the $3e_g \rightarrow 5t_u$ transitions are expected to appear at approximately 12–15 kK. Indeed, $Co(NO_2)_6^{4-}$ and $Ni(NO_2)_6^{4-}$ do have weak bands at 15.5 and 13.6 kK, respectively.[14] While these can be reasonably assigned as d-to-d bands it is not inconceivable that the transition $3e_g \rightarrow 5t_u$ contributes to the observed absorption bands. Such an interpretation does require that the transitions from the e_g orbitals to the ligand orbitals give rise to bands of lesser intensity than those from the metal t_g orbitals. Since there is no precedent on which to estimate the magnitude of the oscillator strengths for metal to ligand transitions originating from the e_g orbitals in octahedral symmetry and since it is well known[44] that relative intensities are considerably distorted in solid-state spectra, such an assignment is at least possible. Furthermore it is in keeping with the over-all band assignments for the series of hexanitrometalates.

Finally, consider the weak band exhibited by the Co^{3+}, Fe^{2+}, Co^{2+}, and Cu^{2+} complexes (for Ni^{2+} the situation is complicated by a d-to-d band in the region of interest). The transition energy is rather insensitive to the central metal along the series Fe^{2+}, Co^{2+}, Cu^{2+}, but the trends $\nu(Rh^{3+})$[45] $>$ $\nu(Co^{3+})$ and $\nu(Co^{2+}) > \nu(Co^{3+})$ are characteristic of ligand to metal transitions. The intensity (ϵ 235 in $Co(NO_2)_6^{3-}$) is indicative of a spin-allowed, orbitally forbidden transition. The excitations $(a_u, e_u) \rightarrow 3e_g$ and $(a_u, e_u) \rightarrow 5t_u$ are both compatible with the above observations, with the former more likely because of its lower energy. A consideration of band widths facilitates the choice. On the basis of the Franck–Condon principle,[46] transitions involving little change in equilibrium internuclear distance should be sharp while a large bond length alteration will produce broad bands. Of the energetically accessible orbitals in Figure 6, only the $3e_g$ orbital has a large effect on bonding. Thus, transitions to the σ-antibonding $3e_g$ orbital should be broad, while excitations not altering the population of $3e_g$ should be sharp. The latter case occurs in the $t_{2g} \rightarrow \pi^*$(ligand) transition of $Fe(bipy)_3^{2+}$.[47] In contrast to the 1-kK band width of $Fe(bipy)_3^{2+}$, the 21-kK band of $Co(NO_2)_6^{3-}$ has a width of 4 kK which is comparable to d-to-d transitions involving the e_g orbital. This suggests that the weak transition observed in all first transition series hexanitro complexes is $(a_u, e_u) \rightarrow 3e_g$. Transitions to the A_u and E_u states arising from such an excitation are orbitally forbidden, but may borrow intensity from the nearby (1 ev or less) T_u state by a vibronic mechanism involving any mode of symmetry τ_g or τ_u. The nearly constant frequency along the series Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} probably results from the competition of two effects. Although the separation of the $3e_g$ and (a_u, e_u) orbitals decreases from Fe^{2+} to Cu^{2+}, the excited state electrostatic interaction increases along the same series owing to the increasing population of the $3e_g$ orbital. By way of a general comment, it is to be noted that observation of this unusual forbidden charge-transfer band correlates with the appearance in the MO diagram (Figure 6) of the levels (a_u, e_u) which are absent in the energy level diagram for octahedral symmetry. They are totally oxygen in character and dictated by symmetry to be nonbonding. It is therefore clear that the ultraviolet as well as infrared spectra cannot be satisfactorily explained unless the reduction of symmetry from O_h to T_h by the oxygen atoms is taken into account.

Summary

It is argued that the four intense ultraviolet bands in the spectra of the hexanitro complexes of Fe^{2+}, Co^{2+}, and Ni^{2+} arise from only two configurational excitations, the lower pair being metal to ligand and the latter ligand to metal. A weak band in the vicinity of 22 kK in all spectra is attributed to a forbidden ligand to metal transition from a nonbonding oxygen π orbital

On the basis of extrapolated ligand field parameters it is concluded that no d-to-d spectra are seen for the species $Co(NO_2)_6^{3-}$ and $Rh(NO_2)_6^{3-}$. Rather, the Co^{3+} complex shows a forbidden charge-transfer transition followed by three intense bands which are assigned as $A_g \rightarrow T_u(1a)$, $A_g \rightarrow (T_u(1b), T_u(2a))$, and $A_g \rightarrow T_u(2b)$. For the Rh^{3+} complex the forbidden charge-transfer band has red shifted under the intense bands, leaving only the bands $A_g \rightarrow T_u(1a)$ and $A_g \rightarrow T_u(1b)$ in the accessible ultraviolet.

The spectral interpretation presented here requires that the full localized symmetry of the complexes, T_h, be invoked rather than the idealized symmetry, O_h, one obtains by considering only the nitrogen ligand atoms. Not only is it maintained that certain of the charge-transfer transitions originate from orbitals essentially on the oxygens but also that transitions to excited states which are forbidden in octahedral symmetry (T_{2u}) become allowed states (T_u) in the actual symmetry of the complexes and are observed. To our knowledge, this is the first example of such an effect.

Acknowledgment.—K. G. Caulton gratefully acknowledges a National Science Foundation predoctoral fellowship. This work was also supported by NSF Grant GP-3413.

---

(43) K. Caulton and R. Fenske, to be published.

(44) R. J. H. Clark, *J. Chem. Soc.*, 417 (1964).

(45) The weak band in $Rh(NO_2)_6^{3-}$ is apparently masked by the intense bands in the vicinity of 30 kK.

(46) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957).

(47) R. Palmer and T. Piper, *Inorg. Chem.*, **5**, 864 (1966).