

TABLE III
THE EQUILIBRIUM CONSTANTS OF THE HYDROLYTIC REACTIONS OF BERYLLIUM ION

Equil const	Ref 4	Ref 5	Ref 16	Present work		Final value
				Graphical	HITAC 5020	
$\log * \beta_{1,1}$	< -6.1	$\lesssim -6.0$	-6.01 ± 0.10	$\lesssim -6.0$
$\log * \beta_{1,2}$	-3.24 ± 0.02	-3.22 ± 0.05	-3.22 ± 0.03	-3.60 ± 0.1	-3.66 ± 0.03	-3.66 ± 0.10
$\log * \beta_{3,3}$	-8.66 ± 0.03	-8.66 ± 0.03	-8.664 ± 0.007	-8.70 ± 0.04	-8.75 ± 0.01	-8.75 ± 0.04
$\log * \beta_{2,2}$	-7.1 ± 0.1	-7.15 ± 0.05	-7.15 ± 0.1
$\log * \beta_{2,1}$	-10.9 ± 0.2	...	-10.87 ± 0.04	-10.8 ± 0.1	-10.84 ± 0.05	-10.84 ± 0.1

tion of ionic activity factors with solvent composition still remains uncertain.

The $\text{Be}_2(\text{OH})_2^{2+}$ complex has not been found by the authors quoted above, but some workers have reported the existence of this species.^{17,18} Gilbert and Garrett¹⁸ have studied the complex formation by solubility measurements or, in other words, at the highest Z region. In the present work, the formation of the complex in question becomes more important at higher pH region.

In order to discuss why the values of the stability constants (especially that of the 3:3 complex) in very different solvent systems (or in media of very different macroscopic dielectric constant) agree and how water

(17) M. Prytz, *Z. Anorg. Allgem. Chem.*, **180**, 355 (1929); **197**, 103 (1931); **231**, 238 (1937).

(18) R. A. Gilbert and A. B. Garrett, *J. Am. Chem. Soc.*, **78**, 5501 (1956).

molecules participate in the formation of the complexes, it is necessary to know results in other systems of different composition of aqueous dioxane with the same ionic medium and to estimate the variation of ionic activity factors with composition of the solvent. These studies are in progress in our laboratory and results will be presented in the subsequent papers of this series.

Acknowledgments.—The author wishes to thank Professor Motoharu Tanaka for his great interest and valuable criticism. He is indebted to Professor Hide-take Kakihana, Tokyo Institute of Technology, Tokyo, and Professor Lars Gunnar Sillén and Dr. George Biedermann, the Royal Institute of Technology in Stockholm, for having introduced him to the field of solution chemistry and for much helpful advice.

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Spectroscopic Studies of Some Compounds with Octahedral Polynitrite Anions

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Received December 5, 1966

It is shown that the orange-brown compound previously formulated as $\text{K}_4\text{Ni}(\text{NO}_2)_6$ is a monohydrate. This has been dehydrated but the spectral properties of the red product suggest that the anion is then of the form $\text{Ni}(\text{NO}_2)_4(\text{ONO})_2^{4-}$. The compounds $[(\text{CH}_3)_4\text{N}]\text{Ni}(\text{NO}_2)_6$ and $\text{Cs}_3\text{Mn}(\text{NO}_2)_6$ have been prepared, and the electronic and infrared spectra of these and also $\text{Cs}_3\text{Ni}(\text{NO}_2)_6$ are reported. The pentanitrite complexes contain both nitrogen- and oxygen-bonded nitrite groups, and possible structures are suggested. The trinitrite complex appears to be polymeric with Ni-N(O)O-Ni bridges.

Introduction

Complexes with anions of the type $\text{M}(\text{NO}_2)_x^{n-}$, where M is a first-row transition metal ion, have been long known. From extensive X-ray diffraction studies Ferrari and his co-workers found¹ that most of these compounds have similar structures, in which the six nitrite groups coordinate to M through nitrogen. However, much less is known about anions of stoichiometry $\text{M}(\text{NO}_2)_x^{n-}$ where $x < 6$. We report here the preparation of $\text{Cs}_3\text{Mn}(\text{NO}_2)_6$ and $[(\text{CH}_3)_4\text{N}]\text{Ni}(\text{NO}_2)_6$, the results of spectral studies on these and the compound $\text{Cs}_3\text{Ni}(\text{NO}_2)_6$, and also an unexpected observation concerning the compound previously formulated as $\text{K}_4\text{Ni}(\text{NO}_2)_6$.²⁻⁴

(1) A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **81**, 982 (1951), and references therein.

(2) A. Ferrari, L. Cavalca, and M. Nardelli, *ibid.*, **81**, 945 (1951).

(3) M. Le Postollec and J.-P. Mathieu, *Compt. Rend.*, **264**, 1800 (1962).

(4) M. Le Postollec, J.-P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **60**, 1319 (1963).

Experimental Section

Preparations. $\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$.—This orange-brown compound was obtained by adding a concentrated, aqueous solution of nickel bromide to an excess of a saturated, aqueous solution of potassium nitrite and was dried for several days *in vacuo* over P_2O_5 . *Anal.* Calcd for $\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$: K, 30.71; Ni, 11.53; NO_2^- , 54.24. Found: K, 30.99; Ni, 11.49; NO_2^- , 53.93.

$\text{K}_4\text{Ni}(\text{NO}_2)_6$.—This hygroscopic, red compound was obtained by heating the monohydrate at 100° for several hours. Weight loss: calcd, 3.94; found, 4.00%. *Anal.* Calcd for $\text{K}_4\text{Ni}(\text{NO}_2)_6$: Ni, 11.95; NO_2^- , 56.19. Found: Ni, 11.86; NO_2^- , 55.85.

$\text{Cs}_3\text{Ni}(\text{NO}_2)_6$.—Aqueous solutions of nickel nitrite and cesium nitrite were mixed in 1:3 molar ratio, filtered, and allowed to stand over H_2SO_4 . After several days dark red crystals formed, and these were washed with a little ice-cold water and dried *in vacuo* (5% yield). *Anal.* Calcd for $\text{Cs}_3\text{Ni}(\text{NO}_2)_6$: Ni, 8.54; NO_2^- , 33.46. Found: Ni, 8.57; NO_2^- , 33.16.

$\text{Cs}_3\text{Mn}(\text{NO}_2)_6$.—A methanolic solution of manganese(II) nitrite, prepared from manganese(II) bromide and excess silver nitrite, was added to one of excess cesium nitrite (5:1 molar

ratio). On storing at $\sim 0^\circ$ a cream-colored precipitate was obtained, which recrystallized from methanol as bright yellow crystals (15% yield). The compound slowly decomposed after isolation, but remained unchanged over several months under its mother liquor in a refrigerator. *Anal.* Calcd for $\text{Cs}_3\text{Mn}(\text{NO}_2)_3$: Mn, 8.04; O, 23.41; NO_2^- , 33.65. Found: Mn, 7.83; O, 23.51; NO_2^- , 33.42.

$[(\text{CH}_3)_4\text{N}]\text{Ni}(\text{NO}_2)_3$.—This fawn compound was precipitated when a concentrated, aqueous solution of nickel bromide (0.01 mole) was added to an aqueous solution of tetramethylammonium bromide (0.01 mole) and an excess of sodium nitrite (70% yield, mp 270°). An identical compound was obtained when a large excess of tetramethylammonium bromide was used. *Anal.* Calcd for $[(\text{CH}_3)_4\text{N}]\text{Ni}(\text{NO}_2)_3$: Ni, 21.67; N, 20.68; NO_2^- , 50.94; O, 35.44. Found: Ni, 21.93; N, 20.80; NO_2^- , 50.82; O, 35.15.

Physical Measurements.—X-Ray powder photographs were obtained with an Enraf-Nonius Guinier-DeWolff No. 2 camera using iron radiation. Other measurements were made as described previously.⁵

Results and Discussion

The Compounds $\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ and $\text{K}_4\text{Ni}(\text{NO}_2)_6$.—The orange-brown compound obtained from an aqueous solution of a nickel salt and excess potassium nitrite⁶ has previously been formulated as $\text{K}_4\text{Ni}(\text{NO}_2)_6$, and X-ray² and infrared^{3,4} studies have been made on this basis. However, the infrared spectra of samples of this compound prepared by us showed bands due to water at 3610, 3540, and 1621 cm^{-1} , even after drying *in vacuo* at room temperature over phosphorus pentoxide for several months. Analytical results were consistent with the formulation $\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$.

The X-ray powder pattern of the monohydrate (Table I) could be interpreted in terms of a hexagonal unit cell with $a = 7.634$ Å, $c = 22.45$ Å, and $z = 3$, in good agreement with the results of Ferrari, *et al.*² ($a = 7.63$ Å, $c = 22.42$ Å, $z = 3$), for the compound previously regarded as $\text{K}_4\text{Ni}(\text{NO}_2)_6$. Moreover, the values we observed (Table II) for the N—O stretches, $\nu(\text{N—O})$, and NO_2 deformation, $\delta(\text{NO}_2)$, for $\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ were quite similar to those reported by Le Postollec, *et al.*,^{3,4} for " $\text{K}_4\text{Ni}(\text{NO}_2)_6$."

TABLE I
 d SPACINGS AND RELATIVE INTENSITIES OF
POWDER PATTERN LINES

$\text{K}_4\text{Ni}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$		$\text{K}_4\text{Ni}(\text{NO}_2)_6$	
7.456 ms	2.264 ml	5.939 s	2.418 vw
6.287 s	2.184 ms	5.424 ms	2.347 w
5.655 w	2.166 ms	4.714 vw	2.178 vw
4.262 vw	2.126 w	4.306 w	2.159 w
3.783 s	2.112 w	3.838 ms	2.146 vw
3.689 ms	2.074 vw	3.557 ms	2.020 vw
3.311 w	1.957 vw	3.514 ms	1.997 vw
3.242 m	1.940 w	3.300 m	1.967 vw
3.143 w	1.892 w	3.015 m	
2.867 vw	1.844 w	2.996 m	
2.827 w	1.813 vw	2.854 m	
2.653 vs	1.725 vw	2.728 vs	
2.461 w	1.669 w	2.697 w	
2.420 vw	1.659 vw	2.546 vw	

(5) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).

(6) N. W. Fischer, *Pogg. Ann.*, **74**, 115 (1848).

Although the water in the monohydrate was strongly held at room temperature, the compound could be dehydrated by heating at $\sim 100^\circ$ for several hours. The weight loss was in agreement with the loss of one water molecule, the analytical results for the product corresponded to the formulation $\text{K}_4\text{Ni}(\text{NO}_2)_6$, and the infrared spectrum had no bands due to water. However, the anhydrous compound was dark red, and its X-ray powder pattern (Table I), infrared spectrum (Table II, Figure 1), and electronic spectrum (Table III, Figure 2) differed from those of the monohydrate.

The anhydrous compound was very hygroscopic, and, if exposed to the air, the monohydrate was re-formed. It was, however, quite stable in the absence of water.

From the X-ray work of Ferrari, *et al.*,² the electronic spectrum, and the present and previous^{3,4} infrared studies there is no doubt that all of the nitrite groups in the monohydrate are bonded through nitrogen and the water molecule is not coordinated. In addition to the nitrite infrared bands listed in Table II the monohydrate had a broad band centered at 510 cm^{-1} which was absent in the spectrum of the anhydrous compound. This band, which is probably due to a librational mode of the lattice water, was also observed by Le Postollec, *et al.*,⁴ suggesting, again, that these workers studied the monohydrate.

Dehydration results in a change in the manner of coordination of some of the nitrite groups. The infrared spectrum of the anhydrous compound in the N—O stretching region has, in addition to bands due to nitro groups (at 1325 and 1347 cm^{-1}), bands at 1206 and 1387 cm^{-1} , which may be attributed to nitrito groups.⁵ The spectrum of the anhydrous compound is also more complicated in the $\delta(\text{NO}_2)$ region (Table II), again indicating the presence of more than one type of nitrite group. From these results it appears that the anhydrous compound is of the type $\text{K}_4\text{Ni}(\text{NO}_2)_{6-x}(\text{ONO})_x$.

The electronic spectra of both compounds are typical of octahedral nickel(II). However, although the band energies of the monohydrate are very similar to those of other $\text{Ni}(\text{NO}_2)_6^{4-}$ salts,^{5,7} there is a pronounced decrease in those of $\text{K}_4\text{Ni}(\text{NO}_2)_6$. This weakening of the ligand field about nickel(II) on dehydration is in accord with conversion of some nitro groups to nitrito groups, as the latter occupy a much lower position in the spectrochemical series. From the extent of the reduction in the ligand field, the anhydrous compound probably has the stoichiometry $\text{K}_4\text{Ni}(\text{NO}_2)_4(\text{ONO})_2$.

A possible explanation for the changes in both the crystal lattice and the nature of the complex anion on dehydration is suggested by the structure proposed by Ferrari, *et al.*,² for the monohydrate. Although these workers did not recognize the presence of the water molecule, they found a cavity at the center of the rhombohedral unit cell (*i.e.*, one cavity per formula unit of $\text{K}_4\text{Ni}(\text{NO}_2)_6$). Whereas most of the electrostatic repulsions between the cations were effectively cushioned

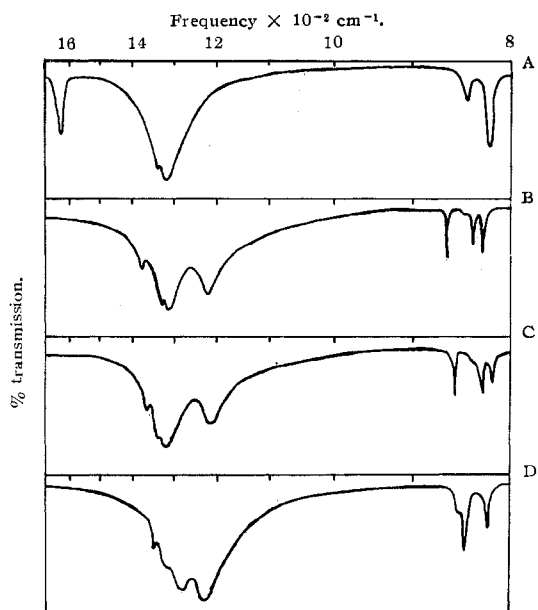
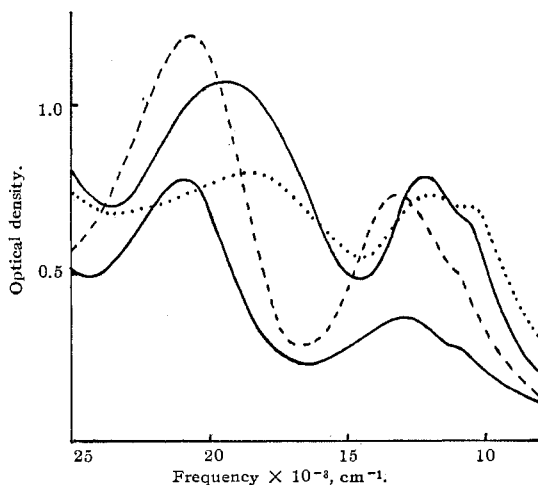
(7) H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

TABLE II
 INFRARED SPECTRA (CM⁻¹) OF SOME M(NO₂)_zⁿ⁻ ANIONS

	$\nu(\text{N-O})$	$\delta(\text{NO}_2)$	ρ_w
K ₄ Ni(NO ₂) ₆ ·H ₂ O	1346 w, 1319 vs	833 m, 810 s	427 m
K ₄ Ni(NO ₂) ₆	1387 m, 1347 w, sh, 1325 vs, 1206 s	867 m, 846 vw, 826 m, 813 m	423 w, 414 m
Cs ₃ Ni(NO ₂) ₅	1372 w, ~1348 vw, sh, 1325 vs, 1208 s	860 m, 833 vs, sh, 821 m, 809 m	433 w, 406 w
Cs ₃ Mn(NO ₂) ₅	1353 w, 1333 vw, sh, 1287 s, 1215 vs	846 vw, 837 m, 811 m	
[(CH ₃) ₄ N]Ni(NO ₂) ₃	1435 s, 1202 vs	852 m	

 TABLE III
 ELECTRONIC REFLECTANCE SPECTRA (CM⁻¹) OF THE COMPLEXES

K ₄ Ni(NO ₂) ₆ ·H ₂ O	20,700, 13,200, ~11,000 sh
K ₄ Ni(NO ₂) ₆	19,200, 12,050, ~10,500 sh
Cs ₃ Ni(NO ₂) ₅	18,300 br, 11,900, ~10,500 sh
Cs ₃ Mn(NO ₂) ₅	21,700
[(CH ₃) ₄ N]Ni(NO ₂) ₃	21,000, 13,250, ~10,900 sh


 Figure 1.—Infrared spectra of: A, K₄Ni(NO₂)₆·H₂O; B, K₄Ni(NO₂)₆; C, Cs₃Ni(NO₂)₅; D, Cs₃Mn(NO₂)₅.

 Figure 2.—Electronic reflectance spectra of: A, K₄Ni(NO₂)₆·H₂O; B, K₄Ni(NO₂)₆; C, Cs₃Ni(NO₂)₅; D, [(CH₃)₄N]Ni(NO₂)₃.

by oxygen atoms from the nitro groups, those between one pair of potassium ions, one on each side of the central cavity, were apparently not. The water molecule in the monohydrate probably occupies this "cav-

ity" and reduces the repulsion between this pair of cations. The increased cation-cation repulsion on dehydration may then be sufficient to change the overall lattice structure.

The reason for the change in the mode of coordination of some of the nitrite groups on dehydration is not clear. The high cation:anion ratio is probably significant, as many anhydrous compounds of the type M^I₂M^{II}Ni(NO₂)₆ are known¹ in which the nitrite groups are apparently all coordinated through nitrogen. In K₄Ni(NO₂)₄(ONO)₂ the need for effective "cushioning" between cations may again be important and may be better achieved if some nitrito groups are present, as in this type of coordination the nonbonded oxygen atom is farther from the metal ion than in the nitro arrangement. It may be noted that the lower frequency N-O stretch attributed to the nitrito groups (at 1206 cm⁻¹) is not reduced from the free-ion value by as much as in some other nickel nitrito complexes (e.g., 1114 cm⁻¹ in Ni(py)₄(ONO)₂⁵). This suggests that the formally nonbonded oxygen atoms of the nitrito groups are affected in a way such as to tend to retain the equivalence of the N-O bonds, and interaction with the cations may bring about this effect.

The Pentanitrite Complexes.—Crystallographic studies have been reported⁸ for the compounds M₃Ni(NO₂)₅ (M = Rb or Cs), but the structure of the anion was not elucidated. We have examined the electronic and infrared spectra of the cesium salt⁹ (Tables II and III, Figures 1 and 2).

The infrared spectrum is quite similar to that of the anhydrous complex K₄Ni(NO₂)₄(ONO)₂ discussed above, with bands which may be assigned to the N-O stretches of both nitro (~1348 and 1325 cm⁻¹) and O-bonded nitrite (1372 and 1208 cm⁻¹) groups. The electronic spectrum is consistent with six-coordinate nickel(II), though the breadth of the band due to ³A_{2g} → ³T_{1g}(F) (there is possibly a shoulder on the high-energy side of this band) and the presence of a pronounced shoulder at ~10,500 cm⁻¹ on the side of the band due to ³A_{2g} → ³T_{2g} may indicate that the ligand field is of lower symmetry than O_h. The ~10,500-cm⁻¹ absorption may, alternatively, be due to ³A_{2g} → ¹E_g. From the energy of the first spin-allowed band, the ligand field in the pentanitrite anion is much less than in the Ni(NO₂)₆⁴⁻ ion and is, in fact, very similar to that in the compound K₄Ni(NO₂)₄(ONO)₂.

The most likely ways in which the nickel ion in Cs₃Ni-

(8) A. Ferrari, M. Nardelli, and G. Bigliardi, *Gazz. Chim. Ital.*, **88**, 827 (1958).

(9) Just before the submission of this paper B. J. Hathaway and R. C. Slade reported [*J. Chem. Soc., Sect. A*, 1485 (1966)] magnetic and spectral studies on Rb₂Ni(NO₂)₅.

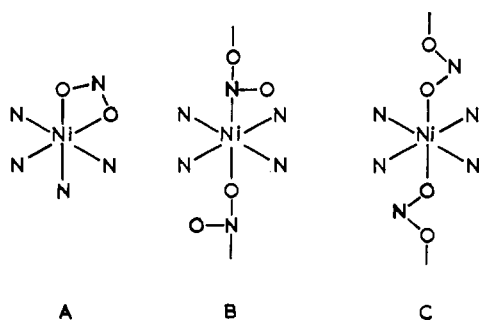


Figure 3.

(NO₂)₅ can attain a coordination number of six, employing both N- and O-bonded nitrite groups, are shown in Figure 3. Bridging of type B is excluded on two counts. First, the ligand field due to a nitrite bridge of this type is almost as strong as that of a unidentate nitro group,¹⁰⁻¹² whereas the ligand field in Cs₃Ni(NO₂)₅ is much weaker than in Ni(NO₂)₆⁴⁻. Second, as discussed below for the compound [(CH₃)₄N]Ni(NO₂)₃, nitrite bridges as in B give rise to a strong ν (N-O) band at ~ 1430 cm⁻¹ or above,^{12,13} which is not found for Cs₃Ni(NO₂)₅.

An unequivocal decision cannot be made between types A and C. Since A lacks a center of symmetry, the electronic bands might be expected to be more intense than those of the Ni(NO₂)₆⁴⁻ ion, whereas they are not. However, this is of doubtful diagnostic value, especially for reflectance spectra.

If the Ni-O bonds in A or C are equivalent, both types of nitrite coordination would be expected to give similar infrared spectra. However, unsymmetric chelation, or the formation of a chain such as C but with nonequivalent Ni-O bonds, would be expected to give an infrared spectrum intermediate in type between that of a symmetrical chelating nitrite and a unidentate nitrito group. Comparison of the N-O stretching frequencies of the O-bonded nitrites in Cs₃Ni(NO₂)₅ (1372 and 1208 cm⁻¹) with those (1289 and 1200 cm⁻¹)¹⁴ of Ni(N,N,N',N'-tetramethylethylenediamine)(O₂N)₂, in which the nitrite groups are chelating,¹⁵ and those

(10) M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Chem. Commun.*, 477 (1965).

(11) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **5**, 1303 (1966).

(12) M. A. Hitchman, Ph.D. Thesis, London University, 1966.

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 154.

(14) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **4**, 721 (1965).

(15) M. G. B. Drew and D. Rogers, *Chem. Commun.*, 476 (1965).

(1387 and 1130 cm⁻¹)⁵ of Ni(N,N-dimethylethylenediamine)₂(ONO)₂¹⁶ suggest that in Cs₃Ni(NO₂)₅ the Ni-O bonds are not equivalent.

The compound Cs₃Mn(NO₂)₅ appears to be the first pentanitrite complex of manganese(II). The infrared spectrum in the N-O stretching region is generally similar to that of the nickel(II) compound (Figure 1), and both N- and O-bonded nitrite groups are probably present. However, there is no δ (NO₂) band corresponding to that observed at 860 cm⁻¹ for the nickel complex, and no bands were found in the region of the M-NO₂ wagging mode (ρ_w). The two pentanitrites were not isomorphous.

A solution electronic spectrum of Cs₃Mn(NO₂)₅ could not be obtained owing to decomposition. Several d-d bands are expected for manganese(II) and these are generally quite weak. However, the reflectance spectrum of Cs₃Mn(NO₂)₅ showed only one rather broad and relatively intense band (optical density ~ 1.0 unit) which may not be d-d in origin.

The Compound [(CH₃)₄N]Ni(NO₂)₃.—This trinitrite complex was obtained even when a large excess of tetramethylammonium nitrite was present in the reaction mixture. The electronic spectrum of this compound (Table III, Figure 2) may be assigned satisfactorily on the basis of octahedrally coordinated nickel(II) [³A_{2g} → ³T_{1g}(F) at 21,000 cm⁻¹, ³A_{2g} → ³T_{2g} at 13,250 cm⁻¹, with the weak shoulder at $\sim 10,900$ cm⁻¹ being probably due to ³A_{2g} → ¹E_g]. From the infrared spectrum (Table II) only one type of nitrite coordination is present, and thus each nitrite must be bidentate. The frequencies of the N-O stretches, 1435 and 1202 cm⁻¹, and particularly the high value observed for the former, are in accord^{12,13} with nitrite bridging of type B in Figure 3. This type of bidentate coordination is also indicated by the high ligand field strength of the nitrite groups in the trinitrite, which, from the frequencies of the spin-allowed bands, is only slightly less than that in the Ni(NO₂)₆⁴⁻ ion.

We conclude, therefore, that there are no discrete anions in [(CH₃)₄N]Ni(NO₂)₃ but that the compound is polymeric, with a three-dimensional network of Ni-N-(O)O-Ni linkages.

Acknowledgments.—We thank the Science Research Council for a Research Studentship (to M. A. H.) and Professor D. Rogers for the use of the X-ray camera.

(16) M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 363 (1964).