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Preparation of Some Nitro-amine Complexes of Nickel and Their Properties

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Diaquobis(ethylenediamine)nickel(II) ion and nitrite ion form a red complex $[\text{Ni}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^+$ of low stability in an aqueous solution. Two kinds of red crystals, i.e. $\text{NiNO}_2(\text{en})_2\text{ClO}_4$ and $\text{Ni}(\text{NO}_2)_2(\text{en})_2$ separate out on evaporating the above solution, the former being formed in the presence of perchlorate ion. Analogous complexes $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$ and $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$ were obtained by using 1,3-diaminopropane(trimethylenediamine, tn) and hexamethylenediamine(hn) instead of ethylenediamine(en). Spectral and magnetic data of these complexes show that, except for $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$ they are all octahedral nitro-complexes of the high spin type. As for $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$ its infrared spectrum shows an NO_2 -bridged structure in agreement with the results of the x-ray analysis.

Introduction

The present authors carried out a series of preparative and spectral studies¹ on the nitroamine complexes of nickel, for example $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$, $\text{Ni}(\text{NO}_2)_2(\text{en})_2$, $\text{Ni}(\text{NO}_2)_2(\text{pn})_2$, $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$ and $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$. Almost at the same time a paper by Goodgame and Hitchman² was published on the same type of nickel complexes. Some of the data obtained by the present authors overlapped with theirs. However, our study includes some different ligands, and also the data on the complex formation equilibrium in solution. These results are presented in this paper.

Experimental Section

Materials. Among the complexes studied $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$, $\text{Ni}(\text{en})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$ and $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$ were prepared after the methods given in the literature.³ The other complexes were prepared in the following way.

(1) $\text{NiNO}_2(\text{en})_2\text{ClO}_4$. To a concentrated solution of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$ a highly concentrated solution of sodium nitrite was added in excess. The resulting deep red solution was evaporated at room temperature in open air, or in a dessicator. Concentration by heating was avoided as far as possible in the preparation, since thermal decomposition easily took place. Flat prismatic yellowish-red crystals separated out from the solution. They were filtered and washed with ethanol.

Anal. Calcd. for $\text{NiNO}_2(\text{en})_2\text{ClO}_4$: Ni, 18.10; C, 14.81; H, 4.97; N, 21.59%. Found: Ni, 18.15; C, 14.34; H, 5.11; N, 21.29%.

(2) $\text{Ni}(\text{NO}_2)_2(\text{en})_2$. Four methods were found to be successful for preparation: (a) A concentrated solution of potassium nitrite was added to the solution of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$. Precipitated potassium perchlorate was filtered off, and the red filtrate was evaporated at room temperature until deep red crystals separated out. (b) In the above preparation $\text{Ni}(\text{en})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ was used instead of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$. (c) To a concentrated solution of nickel acetate, a highly concentrated solution of sodium nitrite was added in excess, and to the resulting dark green solution two moles of ethylenediamine were added per mole of nickel acetate. The solution became deep red, and by spontaneous evaporation of this solution the same rhombic deep red crystals separated out. (d) A theoretical amount of ethylenediamine was added to an aqueous solution of nickel nitrite which was prepared from nickel sulfate and barium nitrite. On evaporating the solution deep red crystals were obtained again. In any of these methods, the obtained crystals were finally washed with ethanol and all the products were identified by comparing their infrared spectra.

Anal. Calcd. for $\text{Ni}(\text{NO}_2)_2(\text{en})_2$: Ni, 21.67; C, 17.74; H, 5.95; N, 31.02%. Found: Ni, 21.32; C, 17.39; H, 5.82; N, 30.22%.

(3) $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$. (a) To an aqueous solution containing one mole of nickel sulfate, two moles of 1,3-diaminopropane(tn) were added, and to the resulting blue solution a concentrated solution of sodium nitrite was added in excess. Fine red crystals separated out. (b) Nickel perchlorate was used instead of

(1) Presented at the annual meeting of the Chemical Society of Japan held at Yokohama, April 1966.

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

(3) H. Grossmann and B. Schück, *Z. anorg. Chem.*, 50, 16 (1906); H. Glaser and P. Pfeiffer, *J. prakt. Chem.*, 153, 300 (1939); Palmer, *Experimental Inorganic Chemistry*, Cambridge, p. 559 (1954); D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 3, 1389 (1964).

nickel sulfate in the above method. The result was the same. Evaporation was unnecessary because this complex was difficultly soluble in water. The product was washed with ethanol.

Anal. Calcd. for $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$: Ni, 19.66; C, 24.13; H, 6.75; N, 28.14%. Found: Ni, 19.47; C, 23.16; H, 6.63; N, 28.12%.

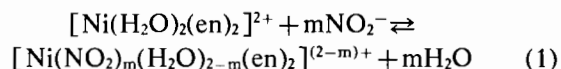
(4) $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$. To an aqueous solution containing one mole of nickel nitrite, an ethanolic solution of two moles of hexamethylenediamine(hn) was added. Bluish precipitate formed immediately which became red after standing for about 2 days. Fine red crystals obtained by filtration were washed with ethanol.

Anal. Calcd. for $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$: Ni, 14.65; C, 35.93; H, 8.54; N, 20.95%. Found: Ni, 14.91; C, 35.94; H, 8.21; N, 20.98%.

Measurements. The visible and ultraviolet absorption spectra of aqueous solutions were determined with a Hitachi EPU-2A photoelectric spectrophotometer and a JASCO ORD/UV-5 self-recording spectrophotometer using quartz cells of 10 mm thickness. The diffuse reflectance spectra were determined with the same Hitachi spectrophotometer equipped with a reflectance attachment, with magnesium oxide as the reference standard. The infrared spectra between 4000 and 400 cm^{-1} were determined with a JASCO DS-402G grating spectrophotometer, using Nujol and hexachlorobutadiene mulls. Magnetic moments were determined by the Gouy method.

Results and Discussion

(1) *Complex formation equilibrium between $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$ and nitrite ions in aqueous solution.* When a concentrated solution of sodium nitrite is added gradually to an aqueous solution of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$, the bluish violet color of the complex solution becomes reddish, and finally a deep red solution is obtained. This color change was already pointed out by Jørgensen,⁴ but a quantitative study has never been made yet. If this red solution is diluted with water, the original bluish violet color reappears. Therefore, the following equilibrium seems to exist in solution:



To find the number m and the formation constant K of the red complex defined as.

$$K = \frac{[\text{Ni}(\text{NO}_2)_m(\text{H}_2\text{O})_{2-m}(\text{en})_2]}{[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2][\text{NO}_2]^m}, \quad (2)$$

the visible absorption spectra of a series of solutions containing 0.05M $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$ and various amounts of nitrite ion were determined at 25°C. The curves are shown in Figure 1; the number on each curve denotes the ratio r of the concentration of nitrite

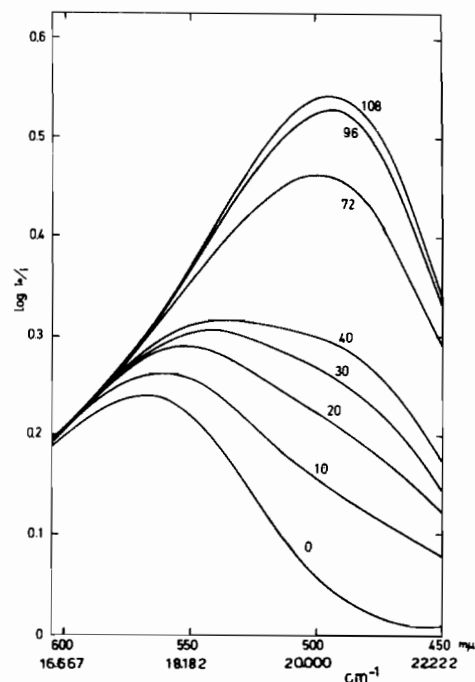


Figure 1. Absorption spectra of the mixed solutions of NaNO_2 and $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$. The figures near the curves indicate the ratio r of the concentration of the former versus that of the latter.

ion versus that of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$ in the respective solutions. A continuous change of the absorption spectrum is shown from $r=0$ to $r=108$, the absorption maximum being shifted from 570 $\text{m}\mu$ to 495 $\text{m}\mu$. If it is assumed that at $r=108$, i.e. at the highest concentration of nitrite ion added, almost all the $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2]^{2+}$ ions in solution are converted into the red nitroamine complex, it is possible to calculate the composition of the solution corresponding to each curve. The data thus calculated lead to the values of $m=1$, and $K=0.51$ which fit well the equation (2) for the range $r=10-40$. Therefore, the red complex is to be formulated as $[\text{Ni}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^+$; the small value of K indicates that the coordination of NO_2^- ligand in this complex is very weak, and it is readily replaced by a water molecule when diluted. The existence of another band at 895 $\text{m}\mu$ with a shoulder at 822 $\text{m}\mu$ in the absorption spectrum of this complex which is shown in Figure 2 indicates its octahedral structure of the high spin type, supporting the formula given above.⁵

(2) *Formation and preparation of the solid complexes.* In view of the low stability of the red complex described above, it is somewhat strange that, by spontaneous evaporation in open air or in a desiccator, red crystals of the complex $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$ are separated gradually from a solution containing $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$ and a large excess of sodium nitrite. On the other hand, if potassium nitrite is

(5) As for the relationship between the spectra and structures of the nickel complexes see, for example, W. Manch and W. C. Fernelius, *J. Chem. Educ.*, 38, 192 (1961). One more absorption band which is expected to exist in the near ultraviolet region could not be observed due to the overlapping of strong absorption of the nitrite ion.

(4) C. K. Jørgensen, *Inorganic Complexes*, Academic Press, p. 84 (1963).

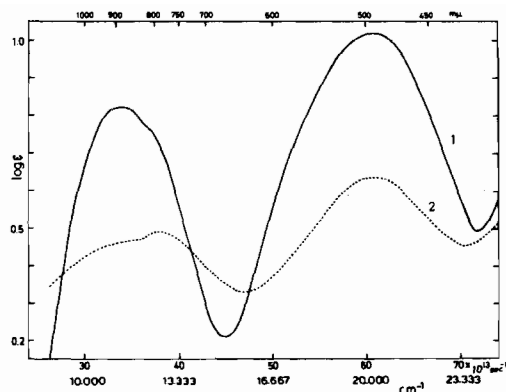


Figure 2. Absorption spectrum of the mixed solution of $[\text{Ni}(\text{H}_2\text{O})_2(\text{en})_2](\text{ClO}_4)_2$ and NaNO_2 in the ratio of 1:108. This spectrum corresponds to that of $[\text{Ni}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^+$ ion. The dotted curve indicates the solid reflectance spectrum of $\text{Ni}(\text{NO}_2)(\text{en}_2)\text{ClO}_4$ shown as the reference, the ordinate being in the arbitrary scale.

used instead of sodium nitrite, and the precipitating crystals of potassium perchlorate are filtered off, the solution yields deep red crystals of $\text{Ni}(\text{NO}_2)_2(\text{en})_2$ on evaporation. Three other methods of preparing this red complex were already given in the above section.⁶ In all these preparative methods a large excess of nitrite ion was always present in solution. It is, therefore, natural to presume the formation of the complex $[\text{Ni}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^+$ first, and then the substitution of a water molecule by an added anion (NO_2^- or ClO_4^-) which leads finally to the formation of $\text{Ni}(\text{NO}_2)(\text{en})_2\text{X}$. Actually, however, the structures of these two complexes having NO_2 and ClO_4 as X are quite different (see later).

By using 1,2-diaminopropane(pn) instead of ethylenediamine, similar red crystals with approximate compositions of $\text{Ni}(\text{NO}_2)_2(\text{pn})_2$ and $\text{Ni}(\text{NO}_2)(\text{pn})_2\text{ClO}_4$ were obtained under similar experimental conditions; however, products of sufficient analytical purity could not be obtained. 1,3-Diaminopropane(tn) gave a similar red complex $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$; being difficultly soluble in water only this complex was precipitated even when

there were perchlorate ions in solution. Hexamethylenediamine(hn) also gave an analogous complex $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$ which was insoluble in water. The last complex may have a polymeric structure involving bridging diamine ligands, although definite experimental evidence has not been found yet.

(3) *Properties of the solid complexes.* The four complexes of en, tn, and hn described above are red crystals of slightly different tones, and they are nearly insoluble in most organic solvents, but, except for $\text{Ni}(\text{NO}_2)(\text{hn})_2 \cdot \text{H}_2\text{O}$, they are more or less soluble in water to give blue solutions, indicating the reverse reaction of the equation (1). Their magnetic moments are as follows at 20-21.5°C: $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$, 2.88 B.M.; $\text{Ni}(\text{NO}_2)_2(\text{en})_2$, 3.01 B.M.; $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$, 3.10 B.M.; $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$, 3.12 B.M. These values indicate that they are octahedral complexes of the high spin type.

The solid reflectance spectra of these complexes are shown in Figure 3 and Table I. They have three d-d bands at ca. 340, 500 and 800 mμ. For all of them, the band at 340 mμ is very broad, the exact wavelength

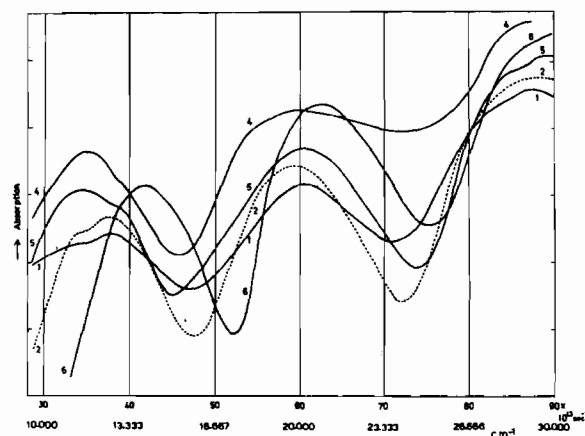


Figure 3. Solid reflection spectra of (1) $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$, (2) $\text{Ni}(\text{NO}_2)_2(\text{en})_2$, (4) $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$, (5) $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$, and (6) $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$. The curve numbers correspond to those in the Table I.

Table I. Visible and Ultraviolet Absorption Bands

Complexes	Wave number (in $\times 10^3 \text{ cm}^{-1}$) and wavelength (in $\text{m}\mu$)				State
(2) $\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$	2.89	20.1	12.5	11.1×10^3	Solid
	345	497	800	900	
(1) $\text{Ni}(\text{NO}_2)_2(\text{en})_2$	29.4	19.7	12.5	11.5	Solid
	340	508	800	870	
(3) $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$	29.4	19.7	12.2	11.5	Solid
	340	508	820	870	
(4) $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$	29.6	19.8	12.6	12.0	Solid
	338	505	794	833	
(5) $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$	30.0	20.0	12.8	11.4	Solid
	333	500	781	877	
(6) $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$	30.0	20.6	13.7	—	Solid
	333	485	730	—	
(7) $[\text{Ni}(\text{NO}_2)(\text{H}_2\text{O})(\text{en})_2]^+$	—	20.2	12.2	11.3	Aq. soln.
	—	495	822	895	

(6) Another method of preparing $\text{Ni}(\text{NO}_2)_2(\text{en})_2$ which is somewhat more complicated than those given here was formerly reported by A. V. Babaeva and S. K. Chang, *Zh. Neorg. Khim.*, 5, 2174 (1960). The formation of

$\text{Ni}(\text{NO}_2)(\text{en})_2\text{ClO}_4$ has also been noted by Curtis (thesis cited by F. J. Llewellyn and J. M. Waters, *J. Chem. Soc.*, 3845 (1962)).

of the absorption maximum being difficult to be located. The band at 800 μ is split into two components. The general features of these absorption curves indicate again the essentially octahedral complexes of the high spin type. Furthermore these absorption curves are quite similar to those of $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$ and $\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$; the similarity is especially remarkable for the former amine complex, while the latter hexanitro complex shows three bands at somewhat shorter wavelengths. Now the structures of these two complexes were already elucidated by Porai-Koshits *et al.*⁷ using the X-ray analysis and infrared spectra. According to them $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$ has the *trans*-dinitro structure and $[\text{Ni}(\text{NO}_2)_6]^{4-}$ has the hexanitro structure. It is, therefore, fairly certain that the complexes $\text{Ni}(\text{NO}_2)_2(\text{en})_2$, $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$ and $\text{Ni}(\text{NO}_2)_2(\text{hn})_2$. H_2O are all nitro complexes, not nitrito complexes, and they probably have the *trans* structures. This conclusion is also borne out by the fact that the d-d bands of these complexes are at much shorter wavelengths than those of the related dinitrito nickel complexes which were reported by Goodgame and Hitchman.^{2,3} For $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$, however, the coordination of an NO_2^- ion and two en molecules to a nickel ion will leave one coordination site vacant, and as is shown in the infrared spectra (Table II) the perchlorate ion is not coordinated as the ligand. Consequently the bridge formation such as shown in Figure 4 should take place.

Table II. Symmetric and antisymmetric stretching vibration frequencies of NO_2^- ions in the complexes (cm^{-1})

Complexes	ν_s	ν_{as}	Source
$\text{NO}_2^-(\text{NaNO}_2)$	1261 vs	1328 m	present study
$\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$	1256 s	1387 m	»
$\text{Ni}(\text{NO}_2)_2(\text{en})_2$	1302 vs	1368 m	»
$\text{Ni}(\text{NO}_2)_2(\text{tn})_2$	1284 s	1354 s	»
$\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$	1290 s	1375 m	»
$\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$	1303 s	1357 s	»
$\text{K}_2\text{Ba}[\text{Ni}(\text{NO}_2)_6]$	1307 vs	1344 sp, w	Goodgame <i>et al.</i> (ref. 2)

vs: very strong; s: strong; m: medium; w: weak; sp: split.

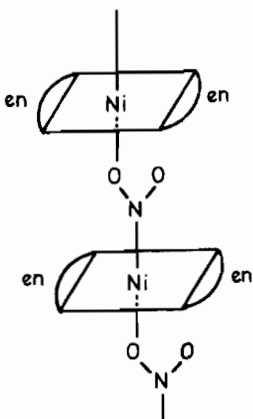


Figure 4. Structure of $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$.

In fact Drew *et al.*⁸ confirmed recently the existence of such a structure by the X-ray analysis. According to the spectrochemical series the absorption bands of $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$ of such a structure are expected to be shifted somewhat to longer wavelengths compared with the complex $\text{Ni}(\text{NO}_2)_2(\text{en})_2$. However, the observed difference between the spectra of these two complexes is remarkably small, and the band at ca. 800 μ is shifted towards the expected direction, while the band at 500 μ is shifted into the opposite direction, presumably due to the distorted shape of the perchlorate complex. It is also noted that the absorption curve of $[\text{Ni}(\text{NO}_2)_2(\text{H}_2\text{O})(\text{en})_2]^+$ in aqueous solution (Figure 2) is quite similar to that of $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$, although a characteristic difference is present in the shapes of the bands at 800 μ .

The infrared spectra of these complexes are quite complicated, but comparing them with those of the complexes like $[\text{Ni}(\text{en})_3]\text{Cl}_2$, $[\text{Ni}(\text{en})_3](\text{ClO}_4)_2$, $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$ and $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ it was possible to find the frequencies which most probably could be assigned to the NO_2^- ions of the studied complexes (Table II) and the ClO_4^- ion of $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$. From these data the following conclusions may be drawn: (1) The ClO_4^- ion in $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$ is almost in a free state, since the frequencies are not essentially changed from those in simple perchlorates. (2) The NO_2^- ions in the three dinitro complexes, *i.e.* $\text{Ni}(\text{NO}_2)_2(\text{en})_2$, $\text{Ni}(\text{NO}_2)_2(\text{tn})_2$ and $\text{Ni}(\text{NO}_2)_2(\text{hn})_2 \cdot \text{H}_2\text{O}$ show the frequencies close to those of NO_2^- ion in $\text{Ni}(\text{NO}_2)_2(\text{NH}_3)_4$. Both of the ν_s and ν_{as} frequencies⁹ are shifted towards higher values by coordination, and this fact supports again their nitro structures. (3) The NO_2^- frequencies in $\text{Ni}(\text{NO}_2)_2(\text{en})_2\text{ClO}_4$ are somewhat different. The ν_s is slightly lowered compared with that of a free NO_2^- ion, while the ν_{as} is shifted strongly to a higher value. This type of change is what Goodgame and Hitchman already expected for a bridging NO_2^- ion which is coordinated through its N atom to one metal, and through its O atom to another.¹⁰ These spectral features are, therefore, in good agreement with the expectation from the structure shown in Figure 4 which had been confirmed by Drew *et al.*⁸

In conclusion the following remark may be of some interest. The NO_2^- ion is classified among those ligands producing the largest ligand field in the spectrochemical series, and it forms stable crystalline complexes with nickel having the expected spectral shifts. Nevertheless only very weak complexes are formed in aqueous solution. These NO_2^- complexes may serve therefore as the striking example showing that the absorption spectrum of a complex is not always a good measure of its stability in solution.

Acknowledgment. The present authors wish to express their gratitude to the Grant-in-aid for the Fundamental Research given by the Ministry of Education.

(8) G. B. Drew, D. M. L. Goodgame, M. A. Hitchman and D. Rogers, *Chem. Commun.*, 20, 477 (1965).

(9) In reference 2 Goodgame and Hitchman assigned the frequencies assuming $\nu_s > \nu_{as}$ and reversing their own previous assignments (cf. ref. 3 and 10). The present authors, however, prefer $\nu_{as} > \nu_s$ according to the advice of I. Nakagawa, University of Tokyo. A more detailed discussion on the NO_2^- frequencies will be published later by him.

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

(7) M. A. Porai-Koshits and L. M. Dikareva, *Kristallografiya*, 4, 650 (1959), *Chem. Abstr.*, 57, 41321 (1962). K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley, p. 153 (1963).