TABLE II

ANALYTICAL DATA FOR HEXACHLORORHENATE(IV) SALTS

Product	% Re Found	% Re Calcd.	% Cl Found	% Cl Calcd.	Cl/Re Found	Cl/Re Calcd.	Av. ox. state Re
K_2ReCl_6	39.25	39.04	43.88	44.58	5.87	6.00	4.00
$ReCl_5$	51.3	51.24	48.0	48.76	4.91	5.00	...
Li_2ReCl_6	44.55	45.23	50.99	51.65	6.01	6.00	3.97
Na_2ReCl_6	40.83	41.87	47.18	47.81	6.07	6.00	3.95
Cs_2ReCl_6	28.48	28.03	31.94	32.00	5.81	6.00	4.04
	28.72		31.13				
	28.45						
Ag_2ReCl_6	30.52	30.31	34.52	34.61	5.94	6.00	3.82
Tl_2ReCl_6	23.05	23.06	26.61	26.33	6.05	6.00	...
	23.02		26.45				
$BaReCl_6$	33.83	34.73	38.83	39.65	6 03	6.00	
$CuReCl_6$[a]	38.44	40.27	45.29	45.99	6.17	6.00	3.93
	38.83						
	38.64						
$CuReCl_6$[b]	36.66	40.27	45.35	45.99	6.50	6.00	3.96

[a] From $Cu(ReO_4)_2$. [b] From $CuReO_4$.

of $CsReO_4$ to Cs_2ReCl_6 and give the product reported. Magnetic moments of 3.2–3.4 B.M. were observed for rhenium in each hexachlororhenate(IV) salt except $CuReCl_6$, for which the value 2.7 B.M. was obtained.

The Na, K, and Cs hexachlororhenate(IV) salts were yellow when freshly prepared and became yellow-green in subsequent manipulations.

Equation 1 does not apply to the conversion of $CuReO_4$ to $CuReCl_6$ by CCl_4. A one to one conversion is assumed in obtaining the calculated yield given in Table I.

Discussion

Following the procedure set forth in this paper it has been possible to prepare hitherto unreported hexachlororhenates(IV) that are more soluble in hydrochloric acid than the chloride of the associated cation. For example, dissolution of Na_2ReCl_6 in concentrated HCl causes precipitation of NaCl and leaves a bright green solution. The precipitation of NaCl was predictable from work reported by the Noddacks[11] in which they attempted the preparation of Na_2ReCl_6 from HCl solution. Four of these salts were prepared, those of Li, Na, Ba, and Cu(II), and were found to be very soluble in water. All four were found to be hygroscopic. The high Cl:Re ratio in the $CuReCl_6$ preparation may indicate the formation of some $CuCl_2$ in the reaction. The procedure also was used to prepare several of the well-known[12] water-insoluble hexachlorohenates(IV), the salts of K, Cs. Ag, and Tl(I).

For the water-soluble group of hexachlororhenates(IV) the analytical values obtained for Re and Cl were consistently low despite the fact that Cl:Re ratios very close to 6 were obtained. Deliberate exposure of Li_2ReCl_6 to moist air for about 5 min. resulted in significant lowering of the percentage of Re and Cl but the ratio of Cl:Re remained the same. The infrared spectrum of $BaReCl_6$ freshly prepared by the method described in this work showed small but definite absorption peaks at 3700 and 1620 $cm.^{-1}$. For O–H in water the stretching and bending vibrations are reported to absorb at 3725 and 1600 $cm.^{-1}$, respectively.[13] Infrared results therefore indicate the strongly hygroscopic nature of the compound. However, available analytical data show a maximum limit of about 2% H_2O in $BaReCl_6$ handled in this manner.

It is of practical significance that this method provides a route to $ReCl_5$ directly from $KReO_4$ (the latter being readily prepared and purified). A yield of 72% of the theoretical calculated from eq. 1 was realized in the $KReO_4$ case.

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Studies of Nitro and Nitrito Complexes. I. Some Nitrito Complexes of Nickel(II)

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The results are reported of studies of the infrared and electronic spectra of the blue or blue-green complexes $Ni(py)_4(ONO)_2$ and $Ni(diamine)_2(ONO)_2$ (where diamine represents one of several C- or N-substituted ethylenediamines). In the solid state these nitrito complexes are quite stable with respect to conversion to the nitro analogs. The antisymmetric and symmetric NO_2 stretching frequencies lie between those of the free ion and those of previously known nitrito complexes such as $[Cr(NH_3)_5(ONO)]^{2+}$. It is suggested that steric factors play an important part in the adoption of oxygen coordination by the NO_2^- ion in contrast with the more usual mode of bonding *via* nitrogen. The electronic spectrum of $K_2Ba[Ni(NO_2)_6]$ is reported and a Δ value of 13,400 $cm.^{-1}$ is obtained from the energies of the ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions.

Introduction

In a previous communication[1] one of us reported the apparently anomalous infrared frequencies due to the NO_2 groups in the blue complex $Ni(a\text{-dieen})_2(NO_2)_2$.[2] Further investigations have shown that in series of compounds of the types $NiD_2(NO_2)_2$ (where D = a C- or

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(1) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

(2) We shall use the following abbreviations for ligands; py = pyridine; en = ethylenediamine; *a*-dimen = N,N-dimethylethylenediamine; *a*-dieen = N,N-diethylethylenediamine; *s*-dieen = N,N′-diethylethylenediamine; *m*-stien = *meso*-1,2-diphenylethylenediamine.

N-substituted ethylenediamine) and $NiL_4(NO_2)_2$ (where L = py or NH_3) two distinct types of complex are formed depending on the identity of the amine ligands. With disubstituted ethylenediamines, and in the case of $Ni(py)_4(NO_2)_2$, blue or blue-green complexes are obtained, while with NH_3,[3] en, or N-monosubstituted ethylenediamines the compounds are red. In this paper we report the results of studies of the infrared and the electronic spectra of the blue complexes and discuss the mode of bonding of the NO_2 groups in these compounds.

Experimental

Preparation of Compounds.—The preparations of the complexes with *a*-dimen and *a*-dieen, except for $Ni(a\text{-dieen})(NO_2)_2$, have been described previously.[1,4]

$Ni(a\text{-dieen})(NO_2)_2$.—The blue complex $Ni(a\text{-dieen})_2(ONO)_2$ was heated in a drying pistol at 116° to constant weight, when a gray-blue solid remained. Calcd. wt. loss for $Ni(a\text{-dieen})_2(ONO)_2 \rightarrow Ni(a\text{-dieen})(NO_2)_2$, 30.34%; wt. loss found, 30.38%.

Anal. Calcd. for $C_6H_{16}N_4NiO_4$: C, 27.00; H, 6.04; N, 20.99. Found: C, 27.18; H, 6.30; N, 20.91.

The complexes with *s*-dieen were prepared by the methods reported[1] for the *a*-dieen analogs. Further details for individual compounds are given below.

$Ni(s\text{-dieen})_2(ONO)_2$.—Blue-green crystals were obtained in 45% yield on recrystallization of the crude complex from ethanol.

Anal. Calcd. for $C_{12}H_{32}N_6NiO_4$: C, 37.62; H, 8.42; N, 21.94; Ni, 15.32. Found: C, 37.57; H, 8.51; N, 21.63; Ni, 15.40.

$Ni(s\text{-dieen})_2(NCS)_2$.—Blue crystals on recrystallization from 1-propanol.

Anal. Calcd. for $C_{14}H_{32}N_6NiS_2$: C, 41.28; H, 7.92; N, 20.64; Ni, 14.41. Found: C, 41.54; H, 7.93; N, 20.81; Ni, 14.27.

$Ni(s\text{-dieen})_2(CCl_3CO_2)_2$.—Blue crystals were obtained in 70% yield from ethanol.

Anal. Calcd. for $C_{16}H_{32}Cl_6N_4NiO_4$: C, 31.20; H, 5.24; N, 9.10. Found: C, 31.25; H, 5.16; N, 8.92.

$Ni(m\text{-stien})_2(ONO)_2$.—Sodium nitrite (0.27 g.) and $Ni(m\text{-stien})_2(ClO_4)_2$ (0.7 g.) were heated in ethanol (200 ml.) The resultant gray-blue crystals were filtered off, washed with hot water and then ethanol, and dried *in vacuo*. The yield was practically quantitative.

Anal. Calcd. for $C_{28}H_{32}N_6NiO_4$: N, 14.61; Ni, 10.20; O, 11.12. Found: N, 14.21; Ni, 10.10; O, 11.30.

$Ni(m\text{-stien})_2(NCS)_2$.—This pale violet complex was prepared in practically quantitative yield by the method described above for $Ni(m\text{-stien})_2(ONO)_2$ using potassium thiocyanate in place of sodium nitrite.

Anal. Calcd. for $C_{30}H_{32}N_6NiS_2$: N, 14.02; Ni, 9.79. Found: N, 14.09; Ni, 9.96.

$Ni(py)_4(CCl_3CO_2)_2$.—Pyridine (4 ml.) was added to a solution of $Ni(CCl_3CO_2)_2 \cdot 4H_2O$ (3 g.) in ethanol (30 ml.). The pale blue complex immediately precipitated and was filtered off, dried *in vacuo* over H_2SO_4, and then recrystallized from 1-propanol. The yield was 60%.

Anal. Calcd. for $C_{24}H_{20}Cl_6N_4NiO_4$: C, 41.18; H, 2.88; N, 8.01; Ni, 8.39. Found: C, 41.59; H, 3.17; N, 7.90; Ni, 8.18.

$K_2BaNi(NO_2)_6$.—An aqueous solution of potassium nitrite was added to one of nickel chloride (0.01 mole) until the orange complex potassium nickel nitrite began to precipitate. Water was then added until the solid just redissolved. The resulting solution was filtered into an aqueous solution of barium chloride (0.01 mole). A buff-colored precipitate was immediately formed. This was filtered off, recrystallized from an aqueous solution of sodium nitrite (0.02 *M*), washed with ethanol and then ether, and air-dried (yield 25%).

Anal. Calcd. for $K_2BaNi(NO_2)_6$: Ba, 24.95; NO_2, 50.17. Found: Ba, 25.01; NO_2, 50.02.

The following complexes were prepared according to methods described in the literature, and had satisfactory analyses: $Ni(py)_4(ONO)_2$[5]; $Ni(py)_4(NCS)_2$[6]; $Ni(m\text{-stien})_2(ClO_4)_2$[7]; $Ni(m\text{-stien})_2(CCl_3CO_2)_2$, blue form.[7] The compound $Ni(py)_4(ONO)_2$ was recrystallized from 1-propanol containing a little pyridine (recovery 80%).

Physical Measurements.—Infrared spectra in the range 2000–400 cm.$^{-1}$ were obtained with a Grubb-Parsons Spectromaster grating spectrometer, and in the range 400–200 cm.$^{-1}$ with a Grubb-Parsons D.M.2 grating spectrometer. The electronic spectra of the solid complexes were measured by the reflectance technique using Unicam S.P.500 and Beckman DK2 spectrometers.

The molecular weight of $Ni(a\text{-dieen})_2(ONO)_2$ was determined in ethyl acetate using a Mechrolab, Inc., Model 301A vapor pressure osmometer. The compound was found to be monomeric under these conditions. Molecular weight observed, 375; calcd. for $C_{12}H_{32}N_6NiO_4$, 383.

Results

Electronic Spectra.—The electronic spectra of the compounds $Ni(py)_4(ONO)_2$ and $NiD_2(ONO)_2$ (D = *m*-stien, *a*-dimen, *a*-dieen, or *s*-dieen) and of the analogous complexes of nickel thiocyanate and nickel trichloroacetate in the solid state were determined over the range 30,000–4000 cm.$^{-1}$. The energies of the band maxima are listed in Table I. The sharp bands in the region 7000–4000 cm.$^{-1}$, due to the vibrational overtones of the organic ligands,[4] have been omitted.

The compounds have spin-triplet ground states and are pseudo-octahedral with ligand fields of D_{4h} or D_{2h} symmetry. In addition to the spin-allowed transitions in the regions 30,000–27,000, 17,500–16,000, and 13,000–7500 cm.$^{-1}$, weak bands or shoulders due to spin-forbidden transitions to levels arising from ^1D and ^1G free ion states were observed in some cases. The highest energy spin-allowed transition was obscured by charge-transfer absorption in the spectra of some of the nickel nitrite complexes. The main features of the spectra of the complexes with *a*-dimen and *a*-dieen have been discussed previously,[1,4] and those with pyridine and the other diamines are rather similar. However, a comparison of the spectra of the blue or blue-green complexes of nickel nitrite with those of the isothiocyanato and trichloroacetato analogs is of importance with regard to the mode of bonding of the NO_2 groups, and this will be discussed subsequently in conjunction with the information from the infrared spectra.

Infrared Spectra.—The three fundamental vibrational modes of the free nitrite ion (C_{2v} symmetry) are all active in the infrared region and have the following

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TABLE I

ELECTRONIC SPECTRA OF THE SOLID COMPLEXES

Compound	Absorption max., cm.$^{-1}$[a]	Ref.
$Ni(m\text{-stien})_2(ONO)_2$	*b*, (~23,300 sh), 17,150, 10,300[c]	*e*
$Ni(m\text{-stien})_2(NCS)_2$	~29,850 sh,[d] 17,700, 11,200[c]	*e*
$Ni(m\text{-stien})_2(CCl_3CO_2)_2$	~29,850 sh,[d] 17,250,[c] 11,900, 9320	*e*
$Ni(a\text{-dimen})_2(ONO)_2$	27,250, 17,300, 10,950, ~8740 sh	4
$Ni(a\text{-dimen})_2(NCS)_2$	27,450, (~22,200 sh), 17,250, (~12,600 sh), 10,400	4
$Ni(a\text{-dimen})_2(CCl_3CO_2)_2$	27,600,[c] 16,650, 11,000, ~8600 sh	4
$Ni(a\text{-dieen})_2(ONO)_2$	*b*, (~20,400 sh), 16,890, (~14,800 sh), 10,350, ~7870 sh	1, 4
$Ni(a\text{-dieen})_2(NCS)_2$	27,550, 17,480, (~15,000 sh), ~11,350 sh, 8910	1, 4
$Ni(a\text{-dieen})_2(CCl_3CO_2)_2$	26,670, 16,340, (~14,100 sh), 9890, ~7550 sh	1, 4
$Ni(s\text{-dieen})_2(ONO)_2$	27,550, (22,500), 17,000, (~12,400 sh), 10,360	*e*
$Ni(s\text{-dieen})_2(NCS)_2$	27,600, 17,400, (~12,500 sh), 10,700	*e*
$Ni(s\text{-dieen})_2(CCl_3CO_2)_2$	27,500, 17,000, (~11,800 sh), 9700	*e*
$Ni(py)_4(ONO)_2$	*b*, 16,900, (~13,000 sh), 10,400	*e*
$Ni(py)_4(NCS)_2$	26,700,[d] (~22,700 sh), 16,700, (~13,000 sh), 10,200	*e*, *f*
$Ni(py)_4(CCl_3CO_2)_2$	26,900,[d] 16,600, (13,100 sh), 9300[c]	*e*
$Ni(NH_3)_4(NO_2)_2$	*g*, 20,350, 19,900, (12,750 sh), 12,000, 11,200	*h*
$Ni(NH_3)_4(NCS)_2$	28,000, 27,900, 17,500, 17,350, (13,000 sh), 10,750	*h*
$K_2BaNi(NO_2)_6$	*b*, 20,620, 13,750	*e*

[a] Spin-forbidden bands in parentheses. [b] Obscured by strong ultraviolet absorption. [c] Asymmetric band. [d] On edge of strong absorption in ultraviolet region. [e] This work. [f] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, London, New York, Paris, 1962, p. 297. [g] Highest energy spin-allowed band not observed. [h] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

frequencies (cm.$^{-1}$) in sodium nitrite[8,9]: antisymmetric stretch (ν_{as}) B_1, 1328 ± 2; symmetric stretch (ν_s) A_1, 1261 ± 3; NO_2 deformation (δ) A_1, 828. The number of infrared active frequencies should not change on coordination either by nitrogen (nitro complex) or by oxygen (nitrito complex).

The spectra of all the nickel nitrite complexes listed in Table I were determined over the range 2000–400 cm.$^{-1}$, and the complex $Ni(a\text{-dieen})_2(ONO)_2$ was also studied down to 200 cm.$^{-1}$. The bands due to ν_{as}, ν_s, and δ for the NO_2 groups were identified by comparison of the spectra of the nickel nitrite complexes with those of the nickel thiocyanate and, in most cases, nickel halide analogs. The absorption frequencies of the –NCS groups are well known. Paramagnetic control compounds were used in all cases, in order to minimize any changes in the frequencies of the vibrational modes of the amine ligands with change in anion.

The bands due to ν_{as}, ν_s, and δ for the nickel nitrite complexes are listed in Table II. The ν_{as} and ν_s bands were strong and could be readily identified; it was generally found that ν_s was somewhat stronger and broader than ν_{as}. The band due to the NO_2 deformation mode was observed as a sharp band of medium intensity in the range 817–825 cm.$^{-1}$. This band could not be identified in the spectrum of $Ni(m\text{-stien})_2(ONO)_2$ due to the presence of *m*-stien absorption in this region. In most cases the absorption arising from the amine ligand varied little with change in anion, though in the complexes with *a*-dimen some of the ligand bands, *e.g.*, those at 1410, 1309, and 1093 cm.$^{-1}$, were somewhat stronger in the spectrum of the nickel nitrite compound than their counterparts in the control compounds.

The compound $Ni(py)_4(ONO)_2$ tends to lose pyridine fairly readily. The spectra of Nujol mulls of the complex show, in addition to the strong bands listed in Table II, weak bands at 1311 and 841 cm.$^{-1}$. These bands disappear when the complex is mulled in pyridine. We have been unable to prepare a pure compound of stoichiometry $Ni(py)_2(NO_2)_2$ but a product approximating to this composition was obtained by heating $Ni(py)_4(ONO)_2$ to 80° in a thermogravimetric balance (Stanton TR-1) until the weight loss corresponded to the change $Ni(py)_4(ONO)_2 \rightarrow Ni(py)_2(NO_2)_2$. Comparison of the infrared spectrum of this product with that of $Ni(py)_2Cl_2$ showed the presence of the following NO_2 bands: 1307 ms, 1217 s, and 841 w cm.$^{-1}$. It appears likely therefore that the complex $Ni(py)_4(ONO)_2$ undergoes some loss of pyridine on mulling in Nujol. Under these conditions a weak band at ~1217 cm.$^{-1}$ should also have been observed, but a band of medium intensity due to pyridine occurs in this region and obscures any absorption due to small amounts of $Ni(py)_2(NO_2)_2$.

TABLE II

Compound[a]	—— NO_2 absorption frequencies, cm.$^{-1}$ ——		
	ν_{as}	ν_s	δ
$Ni(py)_4(ONO)_2$	1393 s	1114 s	825 m
$Ni(a\text{-dieen})_2(ONO)_2$	1361 s	1163 s	824 m
$Ni(a\text{-dimen})_2(ONO)_2$	1387 s	1130 s	817 ms
$Ni(s\text{-dieen})_2(ONO)_2$	1337 s	1205 s	821 m
$Ni(m\text{-stien})_2(ONO)_2$	1350 s	1221 s	*b*
$Ni(a\text{-dieen})(NO_2)_2$	1429 s	1220 s	846, 838 w (?)

[a] Nujol and hexachlorobutadiene mulls. [b] Assignment uncertain due to *m*-stien absorption bands.

The spectrum of $Ni(a\text{-dieen})(NO_2)_2$ could be compared with that of only one control compound, $Ni(a\text{-dieen})(NCS)_2$.[1] Strong bands were observed at 1429 and 1220 cm.$^{-1}$ in the spectrum of the nitrite compound and these have been assigned as ν_{as} and ν_s, respectively. The weak bands at 846 and 838 cm.$^{-1}$ quoted as δ in Table II are only tentative assignments due to the com-

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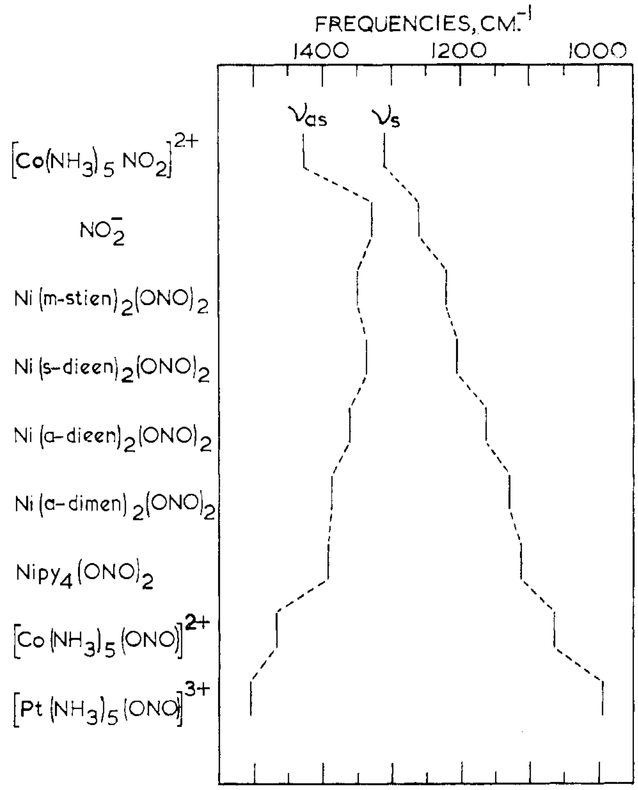

Fig. 1.—Comparison of the NO_2 stretching frequencies of the compounds $Ni(py)_4(ONO)_2$ and $Ni(diamine)_2(ONO)_2$ with those of NO_2^- and of representative nitro and nitrito complexes.

plexity of the spectra in this region and the lack of other control compounds.

Discussion

As a monodentate ligand the nitrite ion may bond either through nitrogen, forming a nitro complex, or through one of the oxygen atoms, forming a nitrito complex. Although nitro complexes are well-known, nitrito complexes are comparatively rare. Studies of the infrared spectra and, in the case of transition metal complexes, electronic spectra have been used by previous workers to identify the mode of bonding in compounds containing coordinated nitrite ions. Both the infrared and the electronic spectra of the blue or blue-green compounds $Ni(diamine)_2(ONO)_2$ and $Ni(py)_4(ONO)_2$ described here are in accord with their formulation as nitrito complexes. We shall first discuss the basis for this conclusion and then its significance in the light of previously published work concerning linkage isomerism by the nitrite ion.

Infrared Spectra.—A considerable quantity of information is available concerning the infrared spectra of nitro complexes.[10,11] The general effect of coordination *via* nitrogen is to raise the frequencies of both $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ from the free ion values of ~1328 and ~1260 cm.,$^{-1}$ respectively, toward the values observed for covalently bound nitro groups, *e.g.*, 1586 and 1377 cm.,$^{-1}$ respectively, in nitromethane.[12] For example, in the case of $[Co(NH_3)_5(NO_2)]Cl_2$ $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ occur at 1428 and 1310 cm.$^{-1}$, respectively, and in $K_2Ca[Ni(NO_2)_6]$ at 1335 and 1325 cm.$^{-1}$.[10]

Coordination *via* oxygen would be expected to raise the frequency of $\nu_{as}(NO_2)$ and to lower that of $\nu_s(NO_2)$ toward the N=O and N—O bond frequencies, respectively, in alkyl nitrites, which for *cis*-methyl nitrite are 1625 and 844 cm.$^{-1}$.[13] Less experimental information is available concerning the NO_2 stretching frequencies of nitrito complexes than for nitro complexes, but the results for $[M(NH_3)_5(ONO)]Cl_2$, M = Cr(III), Co(III), Rh(III), and Ir(III), and for $[Pt(NH_3)_5(ONO)]Cl_3$ are in accord with theoretical expectation.[10,14] The ranges found for the NO_2 stretching frequencies in these nitrito complexes are: ν_{as}, 1505–1460 cm.$^{-1}$, and ν_s, 1060–995 cm.$^{-1}$. One would also expect that the energies of $\nu_{as}(NO_2)$ and, especially, that of $\nu_s(NO_2)$ would provide not only a criterion of the mode of coordination of the NO_2 group, but also, for a series of related complexes, an approximate guide to the strength of the metal–donor atom bond. This has been suggested by Nakamoto and co-workers[15] for nitro complexes. The energy of $\delta(NO_2)$, however, does not seem to change very much from the free ion value in either nitrito or nitro complexes.[10,14]

The values of $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ in Table II are in accord with the presence of nitrito groups in the complexes we have studied except for Ni(*a*-dieen)$(NO_2)_2$, to be discussed subsequently. The $\nu_s(NO_2)$ frequencies are especially revealing in this respect since they all lie between the free-ion value and the position of the $\nu_s(NO_2)$ bands reported[10,14] for the nitrito complexes of the type $[M(NH_3)_5(ONO)]^{n+}$ mentioned above. This is clearly demonstrated in Fig. 1, where the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ values from Table II are compared with those of the free ion and of representative nitro and nitrito complexes.

These results show that the oxygen-bonded nitrite stretching frequencies can fall over a far wider range than previously available experimental evidence would suggest.

This is very apparent when the nitrite stretching frequencies in $[Co(NH_3)_5(ONO)]Cl_2$ are compared with those in Ni(*m*-stien)$_2(ONO)_2$. Although the nature of the perturbation of the nitrite ion is the same in each case, the degree is considerably different, and it is the comparison of the frequencies of the NO_2 group in the complex with those of the free ion which is of value in deciding the method of coordination of the anion.

The infrared spectrum of $K_3Cu(NO_2)_5$ has recently been interpreted[16] as showing the presence of nitro groups only. The main bands reported[16] for the NO_2 stretching frequencies (1351 and 1188 cm.$^{-1}$) lie between those found in the present work for Ni(*a*-dieen)$_2(ONO)_2$ and Ni(*s*-dieen)$_2(ONO)_2$, and we consider that these indicate the presence of nitrito rather than nitro

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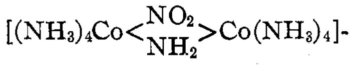
groups in the copper complex. The frequencies found[17] for $K_2PbCu(NO_2)_6$, on the other hand, are those expected for nitro groups.

Further evidence, albeit of a negative kind, for the formulation of the blue nickel(II) diamine compounds as nitrito complexes is afforded by the absence of bands attributable to the wagging mode ρ_w. This is reported to be at 462 cm.$^{-1}$ in $K_2Ca[Ni(NO_2)_6]$[10] and in the range 550–650 cm.$^{-1}$ in some other nitro complexes,[10,11] but is absent in $[Co(NH_3)_5(ONO)]Cl_2$. No absorption due to the nitrite groups was found in the region 400–700 cm.$^{-1}$ in any of the complexes Ni(diamine)$_2$(ONO)$_2$. The compound Ni(*a*-dieen)$_2$(ONO)$_2$ was also studied down to 200 cm.$^{-1}$ but no absorption assignable as ρ_w could be found in this region either.

So far we have discussed only solid state infrared spectra, since nearly all of our results were obtained with Nujol mulls due to a number of reasons. No solvent could be found for the *m*-stien complex. It has already been reported[4] that the *a*-dimen complex exhibits an equilibrium between blue and red forms in solution and we find that the *s*-dieen complex behaves similarly. Studies of these equilibria are in progress at present. Solutions of the compound Ni(*a*-dieen)$_2$(ONO)$_2$ in dichloromethane show no evidence of equilibria of this type, and, under these conditions, the NO_2 stretching frequencies were observed at 1316 and 1131 cm.$^{-1}$. Both of these are lower than their counterparts in the solid state but show that the nature of the coordination of the NO_2 groups remains essentially unaltered. This is also indicated by the electronic spectra.[1]

Previous work has shown[1,18] that the complex Ni(*a*-dieen)$_2$(NCS)$_2$ loses one mole of *a*-dieen on heating to ~160° *in vacuo*, with the formation of Ni(*a*-dieen)(NCS)$_2$, which contains bridging thiocyanate groups.[1] Since the nitrite ion can act as a bridging group, we considered that the formation of the nitrite analog of Ni(*a*-dieen)(NCS)$_2$ would be of interest, both for the confirmation of the nitrite bands in the spectrum of Ni(*a*-dieen)$_2$(ONO)$_2$ and also to supplement the rather meager information available at present concerning the infrared frequencies of bridging nitrites. A compound of stoichiometry Ni(*a*-dieen)(NO$_2$)$_2$ is, in fact, obtained by heating Ni(*a*-dieen)$_2$(ONO)$_2$ to 116° *in vacuo*. Although there is no direct evidence to show that the nitrite groups are functioning as bridging groups in this compound the infrared results suggest that this might be the case. The strong bands at 1361 and 1163 cm.$^{-1}$ in the spectrum of Ni(*a*-dieen)$_2$(ONO)$_2$ are replaced by strong bands at 1429 and 1220 cm.$^{-1}$ in that of Ni(*a*-dieen)(NO$_2$)$_2$. The dearth of information concerning the infrared frequencies of bridging nitrite groups makes a direct comparison with other systems difficult. However, it may be noted that $[(NH_3)_4Co{<}\genfrac{}{}{0pt}{}{NO_2}{NH_2}{>}Co(NH_3)_4]Cl_4\cdot H_2O$ has strong bands at 1485 and 1183 cm.$^{-1}$, which have been assigned to the bridging NO_2 group,[9] compared with bands at 1468 and 1065 cm.$^{-1}$ for the nitrito group in $[Co(NH_3)_5(ONO)]Cl_2$.[10] Hence, the raising of both ν_{as} and ν_s frequencies in Ni(*a*-dieen)(NO$_2$)$_2$ compared with Ni(*a*-dieen)$_2$(ONO)$_2$ may well indicate the presence of bridging NO_2 groups in the former compound. The question of the frequencies of bridging nitrite groups would appear to merit further attention.



Electronic Spectra.—Distinction between nitro and nitrito complexes by means of their electronic spectra rests upon the fact that the two groups $-NO_2$ and $-ONO$ occupy quite different positions in the spectrochemical series.[19] The nitro group exhibits large Δ values and lies between *o*-phenanthroline and the cyanide ion in the spectrochemical series, whereas the nitrito group exerts a much weaker ligand field and is close to carboxylate ions in this series.

In order to determine the value of Δ for nitro groups octahedrally coordinated to nickel(II), we have obtained the solid-state spectrum of $K_2Ba[Ni(NO_2)_6]$. The band positions are listed in Table I. From Liehr and Ballhausen's[20] energy-level diagram for nickel(II) in fields of O_h symmetry we obtain a Δ value of 13,400 cm.$^{-1}$ for the nitro group in the $Ni(NO_2)_6{}^{4-}$ ion. The $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, expected at ~32,000 cm.$^{-1}$, was hidden by very strong charge-transfer absorption in the ultraviolet region. The Δ value found for the $Ni(NO_2)_6{}^{4-}$ ion may be compared with that of 12,000 cm.$^{-1}$ reported[20] for the tris(*o*-phenanthroline)nickel cation.

In centrosymmetric complexes of nickel(II) with D_{4h} or D_{2h} symmetry, the spectral bands due to the spin-allowed transitions from the $^3A_{2g}$ ground state to the states $^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ in O_h symmetry are split. In complexes of the general type NiL_4X_2 the extent of the splitting will, to a first approximation, depend upon the relative Δ values of L and X,[21] and secondly the absolute energies of the bands will provide some measure of the magnitude of the average ligand field environment due to L and X.[19]

This may be seen from the results obtained by Hare and Ballhausen[21] from their studies of the polarized crystal spectra of $Ni(NH_3)_4(NCS)_2$ and $Ni(NH_3)_4(NO_2)_2$. These results are included in Table II for comparison purposes, since the NO_2 groups in $Ni(NH_3)_4(NO_2)_2$ are known[3] to be coordinated *via* nitrogen and in *trans* positions.

As may be seen from Table II, the energies of the bands in the reflectance spectra of the compounds Ni(py)$_4$(ONO)$_2$ and Ni(diamine)$_2$(ONO)$_2$ are all very similar to those observed for their isothiocyanato and trichloroacetato analogs. It can be concluded, therefore, that the effective ligand fields due to the nitrite groups in these compounds are comparable with those due to $-NCS^-$ and $CCl_3CO_2{}^-$.

In contrast with the above, the band energies of $Ni(NH_3)_4(NCS)_2$ are generally similar to those of their di-

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[17] Y. Puget and C. Duval, *Compt. rend.*, **250**, 4141 (1960).

[18] H. Glaser and P. Pfeiffer, *J. prakt. Chem.*, **153**, 300 (1939).

[19] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, London, New York, Paris, 1962, p. 109.

[20] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

[21] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

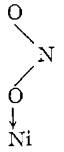
amine analogs, but those of $Ni(NH_3)_4(NO_2)_2$ are at appreciably higher energies, as expected from the relative positions of $-NCS$ and $-NO_2$ in the spectrochemical series.

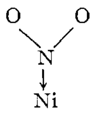
Thus the electronic spectra provide good evidence for the formulation of the compound $Ni(py)_4(ONO)_2$ and the blue compounds $Ni(diamine)_2(ONO)_2$ as nitrito complexes

Comparison with Other Nitrito Complexes.—Apart from one or two isolated cases[22] the only well-characterized nitrito complexes are those of the type $[M(NH_3)_5(ONO)]^{n+}$ where M = Cr(III), Co(III), Rh(III), Ir(III), and Pt(IV).[14] With the exception of the Cr(III) compound, these nitrito complexes rearrange, even in the solid state, to the corresponding nitro compounds. The formation of the unstable nitrito forms has been attributed to the unusual kinetics of formation,[14,23] in which the strong metal–oxygen bond of the hydroxy intermediate $[M(NH_3)_5(OH)]^{n+}$ remains unbroken on attack by N_2O_3. The rearrangement of most of these nitrito complexes to the thermodynamically more stable nitro forms then proceeds by an intramolecular process.

The isolation of the nitrito complexes of nickel(II) studied in the present work demonstrates that the inert nature of complexes of metal ions with d^3 or spin-paired d^6 configurations is not necessarily a prerequisite for the formation of nitrito complexes in general. The cause of the coordination *via* oxygen in the case of the nickel nitrite complexes is almost certainly not the kinetic one mentioned above since the nickel complexes are far too labile and are obtained, moreover, in alkaline solution, which precludes the attack by N_2O_3, as this is formed under weakly acid conditions.

We consider that the most likely explanation for the formation of these stable nitrito complexes is steric in origin. In a complex such as $Ni(NH_3)_4(NO_2)_2$, the four ammonia molecules provide little or no steric hindrance to the approach of the nitrogen atom of the angular nitrite ion. However, with bulky, substituted ethylenediamine ligands occupying four coordination positions in a plane, the axial approach of an oxygen atom as in I may cause less steric hindrance between anion and diamine than nitrogen coordination, as in II. Anion–diamine steric interactions have been shown[4] to play a major part in deciding the spin multiplicities of members of the series $Ni(a\text{-dimen})_2X_2$ and $Ni(a\text{-dieen})_2X_2$. It also appears that when the anion X can coordinate in more than one way with differing spatial requirements, then anion–diamine steric factors may decisively influence the particular structure adopted.


I


II

It is interesting to note that the pyridine rings in $Ni(py)_4(ONO)_2$ provide sufficient steric repulsion to cause the formation of a nitrito rather than a nitro complex, though this is perhaps hardly surprising when it is considered that the pyridine rings in $Ni(py)_4Cl_2$ have been shown to be at an angle of ~45° to the $Ni-N_4$ plane.[24]

Steric interactions between anions and in-plane ligands might be expected to influence not only the mode of coordination of an ion such as NO_2^-, but also the strength of the metal–donor atom bond. If the divergence of the ν_{as} and ν_s NO_2 stretching frequencies from the free ion values is taken as at least an approximate measure of the strengths of the metal–oxygen bonds, then, as may be seen from Fig. 1, the bonding in these nickel(II) compounds is weaker than in the nitrito complexes with the trivalent ions or Pt(IV), as expected. Moreover the Ni–O bond strengths increase in the order: $Ni(m\text{-stien})_2(ONO)_2 < Ni(s\text{-dieen})_2(ONO)_2 < Ni(a\text{-dieen})_2(ONO)_2 < Ni(a\text{-dimen})_2(ONO)_2 < Ni(py)_4(ONO)_2$. This series does indeed parallel the expected steric requirements of the amine ligands, except possibly in the case of *s*-dieen. It is probably significant in this context that in the series of complexes $Ni(diamine)_2X_2$ the tendency for a given complex to have a spin-triplet ground state rather than a spin-singlet ground state also increases in the order[1,4,7]: $Ni(m\text{-stien})_2X_2 < Ni(a\text{-dieen})_2X_2 < Ni(a\text{-dimen})_2X_2$. The magnetic properties of the compounds $Ni(py)_4X_2$ would place them to the right of the *a*-dimen complexes in the above series. However, the markedly weaker ligand field strength of pyridine compared with those of the diamines vitiates direct comparison of this kind, since this effect alone would stabilize a spin-triplet ground state.[25]

In order to confirm that the NO_2 groups in these compounds $Ni(diamine)_2(ONO)_2$ are in fact coordinated *via* oxygen and to examine in detail the geometry of one of the complexes, we are at present carrying out a full X-ray structural study on $Ni(a\text{-dimen})_2(ONO)_2$. The monoclinic unit cell contains two molecules, and the space group is $P2_1/C$. This shows that the molecule is centrosymmetric with the anions in *trans* positions.

It appears likely that the use of ligands such as these substituted ethylenediamines would provide other nitrito complexes. Certainly, if the steric factors are of importance in stabilizing oxygen coordination, then in the case of metal ions with d^3 and spin-paired d^6 electron configurations the combination of the steric and the kinetic factors might well produce stable nitrito compounds. Studies along these lines are in progress.

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