847. *Infrared Spectra of Some Nitrato-co-ordination Complexes.*

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The infrared absorption spectra of a number of nitrato-complexes of metals have been examined in the region between 4000 and 700 cm.$^{-1}$. Assignments have been made for vibrations characteristic of the co-ordinated nitrato-group. Strong absorption bands, which do not occur in ionic nitrates, appear in the regions 1530—1480 and 1290—1250 cm.$^{-1}$. The absorption arising from the vibration ν_1, theoretically inactive for NO_3^- ion, occurs as a strong peak in the nitrato-complexes within the range 1034—970 cm.$^{-1}$, here designated ν_2 and due to $^-O^-NO_2$ stretching.

RECENTLY Shimura and Tsuchida [1] examined some nitratoammino-complexes of tervalent cobalt in the visible and ultraviolet region. However, no data on infrared absorption of nitrato-complexes have been reported. The present work was undertaken to ascertain whether there were features in the infrared spectra which could be used to distinguish co-ordinated nitrato-groups from the nitrate ion in metal complexes.

EXPERIMENTAL

Determination of Spectra.—A Grubb-Parsons double-beam infrared spectrometer, equipped with an S3A monochromator and a rock-salt prism, was used. The samples were ground in an agate vibration mill. The mulling agents used were Nujol (2—15 μ) and hexachlorobutadiene (5—8 μ). The latter was used for the region obscured by Nujol absorption bands.

The samples were examined between rock-salt plates; in cases where it appeared likely that there might be some replacement of a nitrato-group by chloride from the rock-salt plates, the plates used were coated with a fine film of polystyrene, as supplied by Grubb-Parsons.

Preparation of Compounds.—Hexamminocobalt(III) chloride was prepared as described by Gmelin [2] (Found: Cl, 39·7; Co, 22·2. Calc. for $H_{18}N_6Cl_3Co$: Cl, 39·8; Co, 22·0%). From it was prepared hexamminocobalt(III) nitrate by treatment with silver nitrate [3] and subsequent recrystallization (Found: Co, 17·0. Calc. for $H_{18}O_9N_9Co$: Co, 17·0%). Carbonatotetramminocobalt(III) nitrate hemihydrate was prepared as described by Gmelin [4] (Found: Co, 22·7. Calc. for $CH_{12}O_6N_5Co,\frac{1}{2}H_2O$: Co, 22·8%), and *dinitratotetramminocobalt*(III) *nitrate monohydrate* was prepared from it by treatment with nitric acid [5] (Found: Co, 17·6; H_2O, 5·4. Calc. for $H_{14}O_{10}N_7Co$: Co, 17·8; H_2O, 5·4%). Nitratopentamminocobalt(III) nitrate was prepared as described by Gmelin [6] (Found: Co, 17·8. Calc. for $H_{15}O_9N_8Co$: Co, 17·9%). This (0·7 g.) was dissolved in cold water (175 ml.) containing a few drops of nitric acid, and treated with a solution of potassium chloroplatinate(II) (0·9 g.) in water (30 ml.). *Nitratopentamminocobalt*(III) *chloroplatinate*(II) was precipitated as fine pinkish-brown crystals, which were filtered off, and washed with water, then acetone (Found: Cl, 25·7; N, 15·8. $H_{15}O_3N_6Cl_4CoPt$ requires Cl, 26·1; N, 15·5%).

Nitratochlorotetramminocobalt(III) *chloride hemihydrate.* Dinitratopentamminocobalt(III) nitrate monohydrate (2 g.) was treated on a filter-paper with 1N-sulphuric acid (30 ml.), warmed to 30°. The filtrate was allowed to run into ice-cold concentrated hydrochloric acid (100 ml.). The *compound* was obtained as a purplish-pink precipitate, which was washed with ice-cold hydrochloric acid, then acetone (Found: Co, 21·3; Cl, 26·5; N, 25·2; H_2O, 3·9. $H_{12}O_3N_5Cl_2Co,\frac{1}{2}H_2O$ requires Co, 21·9; Cl, 26·4; N, 26·0; H_2O, 3·3%).

Dinitratodiaquopalladium(II). Palladium was dissolved in concentrated nitric acid, and the solution evaporated to small bulk. The mixture was cooled, and the light brown crystals filtered off, pressed almost dry, and dried *in vacuo* over sodium hydroxide (Found: Pd, 40·0. Calc. for $H_4O_8N_2Pd$: Pd, 40·0%).

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[1] Shimura and Tsuchida, *J. Chem. Soc. Japan*, 1956, **77**, 734.

[2] Gmelin, " Handbuch der anorganische Chemie," Verlag Chemie, Berlin, 1930, **58**, *B*, 51.

[3] *Idem, ibid.*, p. 49.

[4] *Idem, ibid.*, p. 279.

[5] *Idem, ibid.*, p. 227.

[6] *Idem, ibid.*, p. 145.

Dinitrato-2 : 2′-dipyridylpalladium(II) was prepared as described by Livingstone [7] (Found: N, 14·0; Pd, 27·2. Calc. for $C_{10}H_8O_6N_4Pd$: N, 14·6; Pd, 27·5%).

cis-*Tetranitratodiamminoplatinum*(IV). *cis*-Dichlorodiamminoplatinum(II), dissolved in dilute nitric acid, was treated with 2 equiv. of silver nitrate. The silver chloride was filtered off, and the platinum oxidized to platinum(IV) by adding concentrated nitric acid and evaporating the solution almost to dryness, pale yellow crystals being deposited (Found: Pt, 40·4. Calc. for $H_6O_{12}N_6Pt$: Pt, 40·8%).

trans-Tetranitratodiamminoplatinum(IV) was prepared analogously (Found: Pt, 41·1%).

Potassium hexanitratocerate(IV). Precipitated ceric oxide was dissolved in hot 8N-nitric acid containing 2 equiv. of potassium nitrate. The solution was concentrated to small bulk and cooled. The *product* was filtered off and recrystallized from 8N-nitric acid. The orange crystals were pressed almost dry and dried *in vacuo* over sodium hydroxide (Found: Ce, 23·1. $O_{18}N_6CeK$ requires Ce, 23·7%).

Dinitratobis(triethylphosphine)nickel(II). A sample of this compound was kindly given by Dr. N. S. Gill (Found: C, 35·5; H, 7·4. Calc. for $C_{12}H_{30}O_6N_2P_2Ni$: C, 34·4; H, 7·2%).

RESULTS AND DISCUSSION

The frequencies of the absorption peaks of the compounds examined are listed in Table 1. The spectrum of hexamminocobalt(III) chloride was obtained for comparison to ascertain which absorption bands arise from the nitrate group in the cobaltammine complexes studied. In the infrared spectrum of $[Co(NH_3)_6]Cl_3$ there are no sharp bands in the vicinity of 825 and 1050 cm.$^{-1}$, where intense absorption occurs in the cobaltammine nitrates. However, there is a strong sharp peak at 1328 cm.$^{-1}$, with two weak shoulders on the higher-frequency side, arising from the symmetric deformation vibration of the NH_3 group. This band is obscured by a strong band when the compounds contain the NO_3^- ion.

The absorption frequencies [9] for the NO_3^- ion, which belongs to the point group D_{3h} (the latter includes all plane trigonally symmetric XY_3 type molecules),[9] are listed in Table 1 together with the vibration types, activity in the Raman and infrared spectra, and assignments.

TABLE 1.

Type [14]	Raman	Infrared	NO_3^-	cm.$^{-1}$	Assignment
A_1'	a	ia	ν_1	1050	N–O stretching
A_2''	ia	a	ν_2	831	NO_2 deformation
E'	a	a	ν_3	1390	NO_2 asym. str.
E'	a	a	ν_4	720	Planar rocking

a = active; ia = inactive.

Miller and Wilkins [10] reported the spectra of ten ionic nitrates [*e.g.*, KNO_3 and $Co(NO_3)_2,6H_2O$], in all of which ν_3 appears very strongly in the range 1390—1350 cm.$^{-1}$, and ν_2 (of medium intensity) in the range 836—815 cm.$^{-1}$. It has been observed by Mizushima and Quagliano [11] that, in addition to the active frequencies for the NO_3^- ion, the forbidden frequency (ν_1) appears in the infrared spectrum of compounds when the nitrate ion is outside the co-ordination sphere. They attribute this to deformation of the ion in the field of the crystal. Calcium nitrate, alone of the nitrates investigated by Miller and Wilkins,[10] shows a weak absorption at 1044 cm.$^{-1}$, which corresponds to the forbidden frequency ν_1 for the nitrate ion. This forbidden frequency in the region of 1050 cm.$^{-1}$ appears weakly in all the complexes containing the free nitrate ion listed in Table 3.

In complexes where the nitrato-group is covalently bound through one oxygen atom, the symmetry is lowered and the group now belongs to the point group C_{2v} and has the vibration types and properties listed in Table 3.

The NO_2 bending and planar rocking vibrations of the ONO_2 group would give

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[7] Livingstone, *J. Proc. Roy. Soc. New South Wales*, 1952, **86**, 35.

rise to frequencies beyond the region observed during this investigation. The above assignments have been made by reference to the spectrum of methyl nitrate.[8]

The strong absorption which occurs in $[Pd(H_2O)_2(NO_3)_2]$ and in $[Ni(PEt_3)_2(NO_3)_2]$ at about 1360 cm.$^{-1}$ can be ascribed to instability of these two complexes leading to some decomposition.

TABLE 2. *Infrared absorption bands.*

	ν_4	NH_3 and $\nu_3NO_3^-$	ν_1	$\nu_1NO_3^-$	ν_2	NH_3 and $\nu_2NO_3^-$	ν_6
$[Co(NH_3)_6](NO_3)_3$		1376s 1299sh		1045w		823s	
$[Co(NH_3)_4CO_3]NO_3,\frac{1}{2}H_2O$		1416sh 1391s 1344sh		1047w		831m 818m	
$[Co(NH_3)_4(NO_3)_2]NO_3,H_2O$	1499s	1393s 1348sh	1266s	1049w	1010s	825m	800w
$[Co(NH_3)_5NO_3](NO_3)_2$	1495s	1377vs 1330sh	1269s	1052w 1032w	1011s	828s	803w
$[Co(NH_3)_4NO_3{\cdot}Cl]Cl,\frac{1}{2}H_2O$	1488s	1387m 1314s	1282s		1013s	825w	797w
$[Co(NH_3)_5NO_3]PtCl_4$	1481m	1362w 1339m 1326m	1269s	1027w	1012s		796s
$[Pd(NO_3)_2$ dipy]	1517s 1502s	1319w	1292sh 1274s 1250sh		989s 979s 975s		801s
$[Pd(NO_3)_2(H_2O)_2$	1502s	1362vs 1307s	1274s		988vs		797sh 784s
$[Ni(PEt_3)_2(NO_3)_2]$	1513m	1418sh 1359vs	1272s		1018s		805m
cis-$[Pt(NH_3)_2(NO_3)_4]$	1529s	1387m 1339w 1326w	1290sh 1276sh 1264s		980s 956s	823s	781w
trans-$[Pt(NH_3)_2(NO_3)_4]$	1522s	1330m	1253s		970bs	821m 816m	
$K_2[Ce(NO_3)_6]$	1531s	1387w	1290s 1277sh		1034vs		804s 799sh
CH_3NO_3	1672vs		1287s		854s		759m

w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, bs = broad, strong, dipy = 2 : 2′-dipyridyl.

Bands at 901 and 904 cm.$^{-1}$ were observed in $[Pd(NO_3)_2(H_2O)_2]$ and *trans*-$[Pt(NH_3)_2(NO_3)_4]$, respectively. These are not assigned at present.

TABLE 3.

Type[14]	Raman	Infrared	ONO_2	cm.$^{-1}$	Assignment
A_1	a	a	ν_3	not obs.	NO_2 bending
A_1	a	a	ν_1	1290—1253	NO_2 sym. str.
A_1	a	a	ν_2	1034—970	N–O str.
B_2	a	a	ν_6	800—781	Nonplanar rock.
B_1	a	a	ν_4	1531—1481	Asym. str.
B_1	a	a	ν_5	not obs.	Planar rock.

The frequency of the N–O stretching vibration would be expected to vary considerably in going from an electrostatically to a covalently bound nitrato-group. The frequency of the absorption band (ν_2) of the nitrato-complexes was found to lie between the extremes, on the one hand, of the observed frequency (1050 cm.$^{-1}$) for an ionic nitrate, and, on the other hand, of the observed frequency (854 cm.$^{-1}$) of covalent $\cdot O{\cdot}NO_2$ in methyl nitrate. In methyl nitrate it is difficult to imagine the $\cdot O{\cdot}NO_2$ group as being anything other than covalently bound, whereas in metal complexes the bonding between the nitrato-group and

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[8] Brand and Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.

[9] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand, New York 1945, p. 178.

[10] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[11] Mizushima and Quagliano, *J. Amer. Chem. Soc.*, 1953, **75**, 4870.

the metal could be regarded as being at least partly electrostatic. This means that the amount of overlap between the orbital of the oxygen of the $\cdot O \cdot NO_2$ group and that of the metal atom is smaller than in the case of a strong covalent bond. Using the frequency of the absorption band (ν_2) as a criterion of the degree of covalent character of the metal–nitrate bond, we obtain the following series: $Ce^{IV} < Ni^{II} < Co^{III} < Pd^{II} < Pt^{IV}$. The results obtained for the compounds $[Pd(H_2O)_2(NO_3)_2]$ and $K_2[Ce(NO_3)_6]$ indicate that in them the nitrato-groups are not purely ionic. Since this work was done the spectrum of $Zn_3Pr_2(NO_3)_6,24H_2O$ has been reported.[12] It displays similar splitting of ν_3 into (*a*) and (*b*) with frequencies 1481—1475 and 1357—1323 cm.$^{-1}$, respectively. The absorption band ν_2 appears at 1047 cm.$^{-1}$. This frequency indicates that the degree of covalent character of the metal–nitrate bond for Pr^{III} is less than that for Ce^{IV}.

The splitting of the bands (ν_4), (ν_1), and (ν_2), observed in [Pd dipy $(NO_3)_2$], arises from the lower symmetry of this compound owing to the two nitrato-groups' being in *cis*-positions; similar phenomena have been observed [13] for *cis*-dinitro-metal complexes.

Finally, strong absorption bands in the regions 1530—1480 and 1290—1250 cm.$^{-1}$ in metal compounds containing an NO_3 group, are indicative that the nitrato-group is co-ordinated to the metal atom.

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[12] Häfele, *Z. Physik*, 1957, **148**, 262.
[13] Gatehouse, unpublished work.
[14] Meister *et al.*, Research Publications, Illinois Institute of Technology, Vol. 6, No. 1, Jan. 1948.