

557. *The Spectra of Some Solid Cobaltic Nitroammines and Certain Other Cobaltic Complexes in the 2—15 μ Region.*

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The infrared spectra of all the available compounds containing the grouping $[\text{Co}^{\text{III}}(\text{NO}_2)_n(\text{NH}_3)_{6-n}]$, which bears a charge of $(3 - n)$ negative units, and of some other related compounds, have been examined in potassium bromide discs. In the intermediate compounds the spectra below 1400 cm.^{-1} depend to some extent upon the stereochemistry of the complex. It is not possible to associate bands in this region with particular ligands.

THE infrared spectra of a number of complex compounds of Co^{III} have been examined previously. However, no systematic study of the effect of the substitution of one ligand by another has been attempted. It is possible to prepare most of the compounds, including some of the isomers, in the series containing the grouping $[\text{Co}^{\text{III}}(\text{NO}_2)_n(\text{NH}_3)_{6-n}]$, the charge on which is $(3 - n)$ negative units. This paper describes the spectra observed in potassium bromide discs between 2μ and 15μ for all the known compounds of this series, and their interpretation insofar as this is possible. Some related compounds were studied to assist in the analysis.

The octahedral arrangement of ligands about a hexaco-ordinated Co^{III} atom is well authenticated. The terminal members of the series, the hexa-amminecobaltic compounds and the cobaltinitrites, both belong to the symmetry group O_h if free rotation occurs about the cobalt-nitrogen bonds. The intermediate members possess a lower degree of symmetry. Geometrical isomers are theoretically possible where $n = 2, 3$, and 4 , the *cis*- being less symmetrical than the *trans*-form. For this reason it has been suggested that the infrared spectrum of the *cis*-isomer of $[\text{Co}^{\text{III}}(\text{NO}_2)_2(\text{NH}_3)_4]\text{X}$ should show more absorption bands

in the 2—15 μ region than the corresponding *trans*-isomer.¹ A detailed interpretation of the spectra is hindered by the fact that it is usually necessary to examine these compounds in the solid, polycrystalline state, where the normal selection rules do not necessarily apply. Further, some fundamental frequencies of an entity containing an atom as heavy as cobalt may lie beyond 15 μ , the normal limit of examination. In amines, the NH_3 ligand attached to a central atom has been likened to a methyl group linked to a heavy organic residue.² Kobayashi and Fujita³ identify the band near 800 cm^{-1} , observed in all amines, as an N-metal stretching frequency, but there is little evidence for this.

To interpret the spectra of these complexes as arising solely from the vibrations of the ligands attached to the central metal atom would imply that the spectra of compounds containing both nitro- and ammine-groups should be (approximately) the sum of the spectra observed for the hexa-ammine and the cobaltinitrite. This is not entirely true. The results for the compounds examined are given in the Table and discussed below in detail for each spectral range.

(i) The N-H stretching bands of amines occur near 3000 cm^{-1} . No fundamental bands would be expected for this region in the spectra of cobaltinitrites. Those observed are presumably due to the presence of a small amount of water. The frequencies recorded for bands in this region are approximate.

(ii) A weak diffuse band, sometimes complex, was found for all the compounds examined, in the region of 1600 cm^{-1} . In the case of amines, this has been variously interpreted as a deformation frequency of the NH_3 group,³ or a degenerate deformation mode of NH_3 attached to a central group.² The precise position of this band is difficult to obtain because of its shape. This may account for the difference between the values obtained in this work (1570 cm^{-1} for $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$) and that of Mizushima *et al.*² (1600 cm^{-1}). A similar band in the spectrum of potassium cobaltinitrite might be assigned to an N-metal stretching frequency, were it not for its high frequency and the observed shift in passing from hexa-amminecobaltic chloride to the corresponding deuterated complex.² The similarity of the two bands must therefore be accidental.

(iii) A strong band in the region of 1400 cm^{-1} in the spectrum of all the compounds examined which contained a nitro-group is absent from those without such a group. In potassium cobaltinitrite it can be resolved into a doublet (1396, 1381 cm^{-1}), and in many of the other compounds containing fewer nitro-groups it is possible to distinguish a shoulder on the low-frequency side of the main band. In two instances the complex contained a nitrate anion. A strong band characteristic of this appeared at a slightly lower frequency (1382—1386 cm^{-1}), without appreciably affecting the band due to the nitro-group in the complex cation. The observed differences in the frequency of this band cannot be associated solely with changes in the groups round the central atom, since appreciable changes occur when the ion outside the complex is changed: 1412 cm^{-1} in $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, and 1430 cm^{-1} in the corresponding potassium salt. In this region there is no distinct band corresponding to the absorption of the ammonium ion. According to Miller and Wilkins,⁴ sodium cobaltinitrite shows a single strong band at a higher frequency (1430 cm^{-1}) than the potassium salt. These authors examined their substances as mulls. The Nujol bands lie on either side of this sodium cobaltinitrite band and it may be for this reason that a doublet was not observed. In simple nitrites, except silver nitrite, no strong band is observed near this frequency. It must therefore be associated with the vibrations of a nitro-group attached to a heavy atom, and the appearance of a rather similar band in the spectrum of silver nitrite⁴ suggests that this is not a simple ionic structure.

(iv) Potassium cobaltinitrite, sodium cobaltinitrite,⁴ and hexa-amminecobaltic chloride¹ all show a single strong band at or near 1330 cm^{-1} . In the case of the last-named compound, the band is identified as the symmetrical deformation frequency of the NH_3 group attached to a heavy atom.² When compounds containing both nitro- and ammine-groups in the complex are examined, some rather complicated absorption

¹ Faust and Quagliano, *J. Amer. Chem. Soc.*, 1954, **76**, 5346.

² Mizushima, Nakagawa, and Quagliano, *J. Chem. Phys.*, 1955, **23**, 1367.

³ Kobayashi and Fujita, *ibid.*, p. 1354.

⁴ Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

bands appear in this region. If one nitro-group is introduced into the complex to form $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ only one band is observed at 1313 cm.^{-1} . In all the other mixed ammine-nitro-complexes two or more bands appear near 1300 cm.^{-1} . The spectrum of *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ shows a pair of widely separated bands ($1319, 1251 \text{ cm.}^{-1}$) very similar in position, though not in shape, to those in the spectrum of *trans*- $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ ($1328, 1266 \text{ cm.}^{-1}$) and *trans*- $\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ ($1323, 1266 \text{ cm.}^{-1}$).

Position of important bands in certain Co^{III} complexes.

Wave-number range (cm. ⁻¹):	>3000	1700—1500	1430	1300
$\text{K}_3[\text{Co}(\text{NO}_2)_6]$	3400	1621	1396	1381
	s.D.	w.D.	s.S.	s.S.
<i>trans</i> - $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$	3300	1630	1412	1323
	s.	s.	s.S.C.	s.S.
<i>trans</i> - $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$	3300	3200	1630	1328
			1430 s.S.	1400 w.S.
			C.	
<i>trans</i> - $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$...	3290	3220	1419	1388 Sh.
		1625		1360
				w.S.
				s.S.
				1328 1320
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{NO}_3$...	3290	3180	1630	1565
			1429 s.	1386 D.*
				1343
				m.S.
				Sh.
				s.
				1326 1316
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$...	3270	3140	1625	1567
			1430	1406
				1374 1358
				1312 1302
<i>trans</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$	3310	3260	1615	
			1423	1407
				1361
				m.S. m.S.
				vs.C.
$[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{NO}_3$	3245	3140	1658	1639
			1608	1382 *
				w.S.
				vs.D.
				1325
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	3219	3243		1570
				w.D.
				1584
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	3273	3163		1426
				w.D.
				1584
				s.S.
				1361
				w.
				1313
Wave-number range (cm. ⁻¹):	1300—1250		900—750	
$\text{K}_3[\text{Co}(\text{NO}_2)_6]$			834	s.S.
<i>trans</i> - $\text{NH}_4[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$		1266	829	s.S.C.
<i>trans</i> - $\text{K}[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$...	1289	w.Sh.	1266	s.S.
<i>trans</i> - $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	1290	s.	1251	w.S.
			829	
				819
				803 Sh.
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{NO}_3$...	1299	s.	1253	w.S.
			849	
				826
				822
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$			844	
				825
				822
<i>trans</i> - $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$...			828	
		1251	vs.D.	
				819
				794 w.S.
$[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{NO}_3$	1285		1268	Sh.
			849	
				833 S.
				827 S.
				769 m.S.
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$			838	m.D.
$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$			841	
				824 S.
				C.

vs. Very strong; s. strong; m. medium; w. weak; S. sharp; D. diffuse; C. complex; Sh. shoulder.

* NO_3^- frequency.

On the other hand, *cis*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$ has two absorption bands, barely resolved, at 1302 and 1312 cm.^{-1} . A similar, more clearly resolved, pair is observed for the corresponding nitrate ($1316, 1299 \text{ cm.}^{-1}$). Unfortunately, *cis*-diamminetetranitrocobaltic compounds have not been prepared. The weak bands at about 1330 and 1250 cm.^{-1} observed in the *cis*-tetramminedinitrocobaltic salts may be due to traces of the *trans*-compounds in the specimens examined. The non-electrolyte, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, which is now known to have the *trans*-configuration⁵ has a pair of strong bands at 1320 and 1290

⁵ Tanito, Saito, and Kuroya, *Bull. Chem. Soc. Japan*, 1952, **25**, 188.

cm.^{-1} in addition to other weaker bands. These strong bands are separated by an amount less than that observed for the above *trans*-compounds and more than that found for the *cis*-compounds.

It might be argued that one of the pair of strong bands observed for all such compounds in this region can be identified with the nitro-, and the other with the ammine-groups, but together they appear to be more characteristic of the complex as a whole. In the case of the dinitrotetra-ammine and tetranitrodiammine salts, their position seems to be governed more by the symmetry class to which the molecule belongs than by its formula.

In almost all the compounds examined which contained both nitro- and ammine-groups a sharp weak band appeared in the neighbourhood of 1360 cm.^{-1} . This did not appear in any of the compounds from which this combination of groups was absent.

(v) Although both cobaltinitrites and cobaltammines, in common with other amines, show absorption bands between 750 and 900 cm.^{-1} , the bands are quite different in appearance. Cobaltinitrites show a strong sharp band at about 830 cm.^{-1} , a similar but apparently weaker band being found in simple nitrites.⁴ Amines such as hexa-ammine- and penta-amminechloro-cobalt chloride, show broad bands of medium strength at 830 — 840 cm.^{-1} . Possible assignments of this band have been given earlier, the best being that due to Mizushima *et al.*² as a rocking mode of the NH_3 group attached to the central atom. The spectra of penta-amminenitrocobalt chloride, and of the salts of the diamminetetranitrocobalt complex, appear to be a simple superposition of the broad ammine band and the sharp band characteristic of the nitro-group. In the spectrum of Erdmann's salt and its potassium analogue, the presence of the broad ammine band is only shown by the skewness of the observed sharp band. The neutral compound has a rather indefinite broad band centred at about 820 cm.^{-1} , the spectrum varying slightly from sample to sample with the mode of preparation. The *cis*- and the *trans*-tetra-amminedinitro-complexes each show a set of three overlapping bands, which however differ markedly in position. Thus, the *cis*-compounds, and tetra-amminecarbonatocobaltic nitrate from which these were made, show a diffuse band of medium strength at 844 or 849 cm.^{-1} overlapping a strong band at 825 or 833 cm.^{-1} , and a weaker band or shoulder at a frequency about 5 cm.^{-1} lower. The *trans*-complex, which does not show the medium-strength diffuse band at 840 — 850 cm.^{-1} , gives two overlapping bands at 828 and 819 cm.^{-1} with a much weaker band at 794 cm.^{-1} . Any attempt to assign these bands in a simple manner to ligand frequencies must fail for such compounds. It should be noted that the similarity observed in the 1300 cm.^{-1} region for the *trans*-tetra-amminedinitro- and diamminetetranitro-complexes is not found in the lower frequency region, between 750 and 900 cm.^{-1} .

The principal points arising from this work are as follows :

(a) Cobaltinitrites and hexa-ammine-cobaltic salts have many similarities in their spectra. In the mixed ammine-nitro-complexes only the strong N—H stretching frequency at above 3000 cm.^{-1} , and a band characteristic of the $-\text{NH}_2$ ligand at 1400 — 1430 cm.^{-1} , can be identified as characteristic ligand frequencies. (b) Frequencies below about 1400 cm.^{-1} cannot be assigned to individual ligands in these mixed complexes, however reasonable this may seem to be for the end members. Both classes of compound have bands in similar positions, especially below this frequency. The absorption bands, especially in the 1300 cm.^{-1} region, are particularly complicated in the intermediate compounds, those with closest similarities being also stereochemically similar. (c) By examining the spectra of the complexes in the 1300 and the 850 cm.^{-1} region, it is possible to distinguish the geometrical isomers of the tetramminedinitrocobaltic complex.

Experimental.—Infrared spectra were measured on a Grubb-Parsons double-beam spectrometer. The specimens were prepared in the form of potassium bromide discs, 1.27 cm. in diameter. A similar disc prepared from the same specimen of potassium bromide was used in the reference beam. The frequencies recorded are not more than 3 — 4 cm.^{-1} in error in the 1300 — 1400 cm.^{-1} region, or more than 1 cm.^{-1} in the 850 cm.^{-1} region.

The complexes studied were prepared by methods described in the literature. Since these compounds are analytically well characterised, and impurities are similar in composition to the required product, it was considered preferable to prepare samples of any given complex by

several different methods and examine their spectra individually, rather than carry out individual analyses. Purification of each sample was also followed by determining the infrared absorption at each stage. The most suitable reference compounds are: $[\text{Co}(\text{NH}_3)_4]^{3-}$, Erdmann's salt, refs. 6, 7; *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ and $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]^+$, ref. 7; $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$, ref. 8.

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⁶ Thomas, "Complex Salts," Blackie and Sons, Glasgow, 1924, p. 116.

⁷ Biltz and Biltz, "Laboratory Methods of Inorganic Chemistry," Hall, Blanchard, Wiley & Sons, New York, 1928, p. 172.

⁸ Jørgensen, *Z. anorg. Chem.*, 1894, 5, 168; 1898, 17, 463.
