concentration of carbon monoxide. An attempt to investigate the effect of added triphenylphosphine on the rate of exchange was not successful. Under these conditions the rhodium(III) compound is readily reduced to the rhodium(I) compound, as shown by the infrared spectrum of the solution. This is a surprising observation, deserving further study, because Vallarino reports that the rhodium(III) compound is not reduced by reducing agents such as hypophosphorous acid and magnesium or zinc powder in ethanol. This may just be due to the insolubility of the rhodium(III) compound in ethanol.

These rhodium(I) and rhodium(III) compounds, like the complexes of platinum(II) and platinum(IV), are low-spin d^8 square-planar and low-spin d^6 octahedral systems, respectively. Substitution reactions of some platinum(IV) complexes are catalyzed by platinum(II) by a two-electron bridged activated complex mechanism.[4] It was found that for the particular system under investigation, rhodium(I) has only a very small effect on the rate of reaction of rhodium(III). This is not too surprising because molecular models show it would be difficult to form the chloro-bridged activated complexes due to the large size of the triphenylphosphine groups. For systems where the bridged complex can be formed, catalysis of rhodium(III) reactions has been observed.[5] Finally, the rate of carbon monoxide exchange in the better coordinating solvent tetrahydrofuran is only approximately four times faster than it is in chloroform. This suggests a general solvent effect rather than a specific solvent displacement type process.

In addition to the compound discussed here, the replacement of carbon monoxide from six-coordinated metal carbonyls has been reported for $Mn(CO)_5X$ (where $X = Cl^-, Br^-, I^-$)[6] and for $Cr(CO)_6$.[7] In every case the reaction proceeds by a dissociation mechanism. It would therefore be of interest to compare the activation energies for these reactions with the metal–carbon bond strengths for the different compounds. The bond strengths are not known, but the infrared spectra give the C–O stretching frequencies, which provide an indication of the metal–carbon bond order. The higher the frequency of the C–O absorption, the lower the metal–carbon bond order. A plot of the activation energies for the replacement of carbon monoxide *vs.* the C–O absorption frequencies[8] for these five metal carbonyls is shown in Fig. 1. This shows that the activation energy for the dissociation of carbon monoxide from a metal carbonyl increases with an increase in the metal–carbon bond order.

Experimental

Materials.—Small samples of $[Rh(P(C_6H_5)_3)_2COCl]$ and $[Rh(P(C_6H_5)_3)_2COCl_3]$ were generously supplied by Dr. Vallarino. Additional material as needed was prepared by the method of Vallarino[1] and of Chatt and Shaw.[9] The compounds were characterized by their analyses and infrared spectra. The quaternary ammonium salt, benzyldimethyl{2-[2-(*p*-1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl}}ammonium chloride (Hyamine 1622) was obtained from Rohm and Haas Chemical Co., Philadelphia, Pa. The radiocarbon monoxide was purchased from Tracerlab, Inc., Chicago, Ill.

Determination of Rates.—The apparatus used and the technique employed were the same as previously described.[10] Also, the same method was used for the treatment of the data observed. In order to make certain that the compound remained unchanged during exchange, the infrared spectra of the solutions were determined before and after exchange. In every case the initial spectrum did not change during the period of carbon monoxide exchange. The spectra were measured on a Baird-Associates Model AB-2 double beam recording spectrophotometer with NaCl optics.

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Contribution from the Department of Chemistry,
Faculty of Science, Tokyo University, Hongo,
Tokyo, Japan, and the Department of Chemistry,
Faculty of Science, Nagoya University,
Chikusa, Nagoya, Japan

Infrared Spectra and Structure of the Hexanitrocobalt Complex Salts

By Ichiro Nakagawa, Takehiko Shimanouchi,
and Kazuo Yamasaki

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The structures of hexanitrocobalt complex salts, $M_3[Co(NO_2)_6]$, have been studied by X-ray analysis.[1] It has been shown that the crystal structure of the K, Rb, and Cs salts is cubic and the molecular symmetry of one complex ion is T_h as shown in Fig. 1a. However, so far no structural analysis has been made for the Na salt.

We have measured the infrared spectra of hexanitrocobalt complex salts and found, as shown in Fig. 2, that the spectrum of the Na salt is different from those of the K, Rb, and Cs salts in the following points. (1) An appreciable difference is observed in the region 1450–1300 cm.$^{-1}$ where the NO_2 stretching vibrations appear. (2) The band near 830 cm.$^{-1}$ is assigned to the NO_2 scissoring vibration. Two sharp bands are observed for the vibration in the spectrum of the Na salt, whereas only one is found for the K, Rb, and Cs salts. (3) A striking difference is observed for the cobalt–nitrogen stretching vibration. The Na

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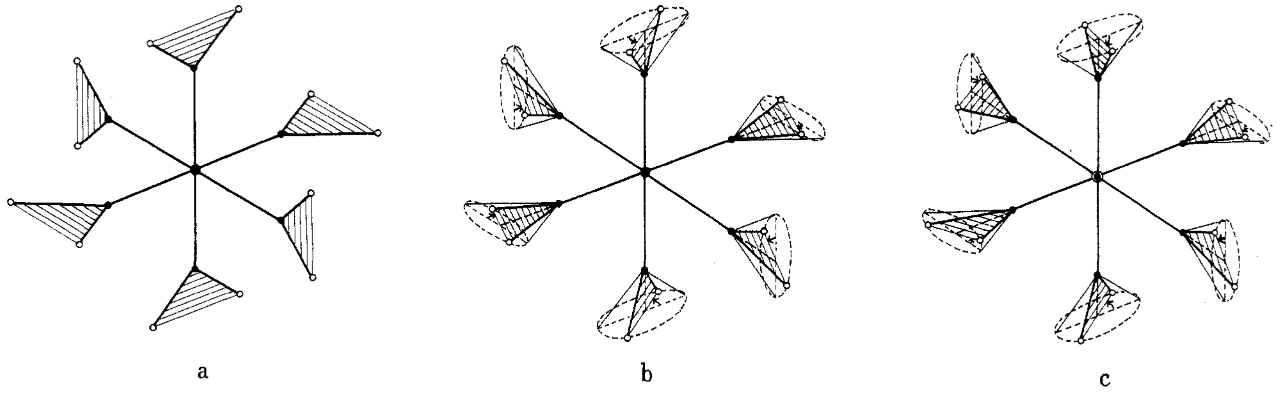

Fig. 1.—Possible structures of $[Co(NO_2)_6]^{3-}$ ion: a, T_h; b, S_6; and c, T symmetries.

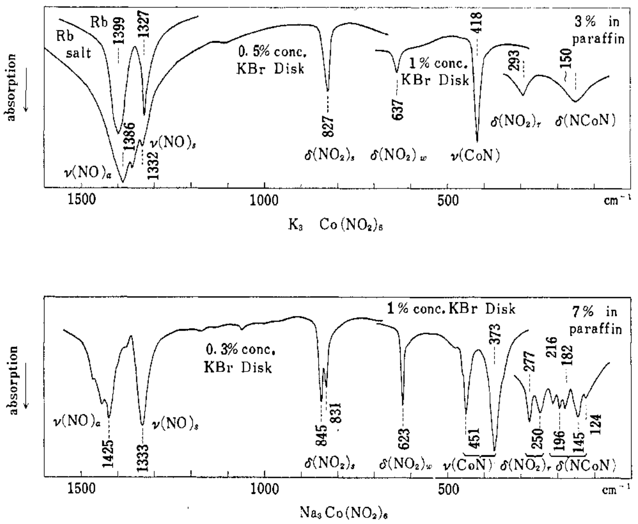

Fig. 2.—Infrared spectra of the hexanitrocobalt complex salts.

salt reveals two strong bands for this vibration, but the K, Rb, and Cs salts have only one band. (4) In the far-infrared region below 300 cm.$^{-1}$ the spectrum of the Na salt is much more complicated than those of the K, Rb, and Cs salts.

These differences in the spectra are too large to be explained by the simple outer ion effect. We may also deny the possibility of the nitrito complex for the Na salt, because the nitrito complex should have its characteristic strong band near 1050 cm.$^{-1}$.[2,3] Therefore, we may naturally expect the difference in the molecular structure of one complex ion.

The molecular symmetry of T_h is of high symmetry. If the NO_2 plane rotates about the Co–N axis starting from the structure shown in Fig. 1a, the symmetry goes down ond we may have two possible structures whose symmetries are S_6 and T as shown in Fig. 1b and 1c. The infrared-active vibrations for each structure are shown in Table I. From this table the spectrum of the K, Rb, and Cs salts is reasonably explained on the basis of the structure of T_h symmetry which has been determined by X-ray analysis. The spectrum of the Na salt is consistent with the S_6 symmetry but not with the T symmetry, because for the latter structure we should observe only one band for the Co–N stretching and NO_2 scissoring vibrations instead of two.

TABLE I

INFRARED-ACTIVE VIBRATIONS OF $[Co(NO_2)_6]^{3-}$ ION FOR THE MOLECULAR SYMMETRIES T_h, S_6, AND T

Vibration modes	T_h	S_6			T	Expected freq. region, cm.$^{-1}$
	F_u	A_u	E_u	Total no.	F	
NO_2 anti. stretching	1	1	1	2	2	1300–1450
NO_2 sym. stretching	1	1	1	2	1	
NO_2 scissoring	1	1	1	2	1	800–850
NO_2 wagging	1	1	1	2	2	600–650
Co–N stretching[a]	1	1	1	2	1	350–500
NO_2 rocking[a]	1	1	1	2	2	250–350
NO_2 twisting[b]	0	1	1	2	1	...
NCoN deformation	2	2	2	4	3	<300

[a] The Co–N stretching and NO_2 rocking modes are coupled with each other. [b] The band due to the twisting vibration may be very weak even for the active species.

A normal coordinate analysis shows that twisting the NO_2 planes by 30° causes the A_u and E_u frequencies of the Co–N stretching vibration to split about 70 cm.$^{-1}$.[4]

Experimental

Measurement of Spectra.—The spectra in the NaCl region were obtained by using a Hitachi EPI-2 infrared spectrophotometer. The wave length calibration was made by using the sharp peaks of indene, 1,2,4-trichlorobenzene, and polystyrene. A Perkin-Elmer 112G foreprism-grating spectrophotometer was also used to determine more precise wave numbers for the sharp peaks. The spectra in the low-frequency region (700–250 cm.$^{-1}$) were obtained by using a CsBr foreprism-grating spectrophotometer designed and adjusted by Shimanouchi, *et al.*[5] The wave length calibration was made by using the pure rotational lines of H_2O vapor and the sharp peaks of 1,2,4-trichlorobenzene.[5] Samples were prepared for examination by the Nujol mull and KBr disk methods. It should be noted that the frequencies for the KBr disk agree with those for the Nujol mull. The spectra in the far-infrared region (300–80 cm.$^{-1}$) were obtained by using a Type FIS-1 Hitachi far-infrared spectrophotometer. Samples were prepared for examination by mixing in paraffin.

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