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The Nature of Bonding and Structure of Pentacyanonitrosylcobaltate(III) on the Basis of Infra-red and Electronic Spectroscopy[a]

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The pentacyano-nitrosylcobaltate(III) previously considered as having the NO-group formally bound as NO^-*, has been investigated. The infra-red and electronic spectra have been measured, and the results of the investigation were discussed. The investigated complex has been reformulated as* $[(CN)_5Co(N_2O_2)Co(CN)_5]^{6-}$ *with* cis *or skew hiponitrite bridging group. The appearance of* $\nu(NO)$ *stretching frequency at about 1770-1860 cm*$^{-1}$ *in dilute solution was assumed as an evidence of equilibrium between monomeric and dimeric forms of the complex.*

Introduction

Unusual properties of the nitrosyl ligand have been subjected to many discussion and controversial opinions. On the basis of its physico-chemical properties and particularly on the basis of infra-red spectra, a number of possible NO group coordination type by the transition metals have been suggested, that is as NO^+, NO^0, NO^- or as a bridging one $> N{=}O$.[2-18] The coordination of the nitrosyl group in nitrosylcyanate cobalt complexes was generally supposed to be as the NO^- ion. Jeżowska-Trzebiatowska and Ziółkowski, however, in their recent works[18] based on studies of infra-red spectra and radioisotopic exchange, on comparing their own results with those for the other nitrosylcyanate transition metal complexes (Cr, Mn, Fe) pointed out the possibility of an alternative NO^- coordination group in the cobalt complex through a bonding similar to the olefinic one. Since the possibility of existence of such a bonding for the NO group seemed to be not quite probable we have undertaken an extensive study reported in the present paper.

Experimental

The cyanonitrosyl complex of cobalt(III) has been prepared by the method given by Nast.[1] The infra-red spectra were recorded from 4000 to 200 cm^{-1} using a Perkin-Elmer Model 621 Spectrophotometer. The IR studies of the aqueous solutions containing the cobalt complex were carried out for water deuterium oxide, and a mixture of $D_2O : H_2O = 1 : 1$; plates of KRS-5 and As_2S_3 were applied. The complex concentrations in aqueous solutions (0.15g per 1.0 cc and 0.20g per 1.0 cc of solution) were enough but, at lower concentrations, the interesting bands were masked by the strong water absorption.

The electronic absorption spectra of the aqueous solutions and the diffuse reflectance spectra of the solid were obtained by using Unicam SP 500 and SP 700 and Specord UV VIS -Zeiss - Jena Spectrophotometers, by applying magnesium oxide as diluting agent.

The magnetic measurements were made by the Gouy and Faraday methods both for complex in the solid phase and in aqueous solutions.

Results and discussion

The infra-red spectra of cyano-nitrosylcobaltate(III) in the solid state, compared to those of hexacyanato-

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cobaltate(III), are presented together with their band assignments in Table I and Fig. 1.

Table I.

$K_3[Co(CN)_6]$	$K_6[Co_2(CN)_{10}N_2O_2]$	Assignments
—	3450 vs,b	ν(OH)
	2200 sh,vw	
	2172 m	
2143 sh,w ?	2150 sh,w ?	
2129 vs	2125 vs	ν(CN)
2120 sh,s	2088 m	
	2068 sh,vw	
	2045 m	
	1621 m	δ(HOH)
	1399,1336 s	ν(NN)
	1043 m	ν_{as}(NO)
	961 m	
	831 s	ν_s(NO)
	599 m	ν(CoN)
564 s	559 s	δ(CoCN)
	537 w	δ(NNO)
	450 w	ν(CoO)
419 vs	411 vs	ν(CoC)
407 vs	380 m	
	281 w	δ(NCoC) or δ(CoNO)

Table II.

Compound	ν(NN)	ν_{as}(NO)	ν_s(NO)	Ref.
$K_6[Co_2(CN)_{10}N_2O_2]$	1336-1399	1043	831	present work
$[NaNO]_n$	1314	1047	830	19
$[NaNO]_2$	1312	1042	837	23
$[KNO]_2$	1304	1057	857	23
$[N_2O_2]^{2-}$	1383	1115	863	20

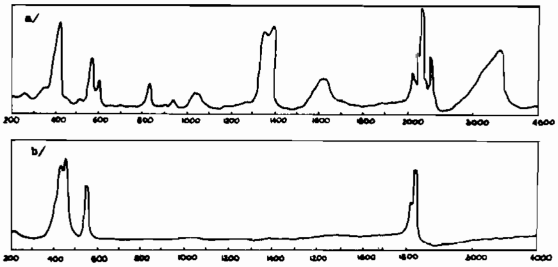
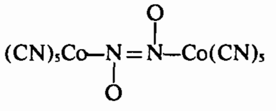


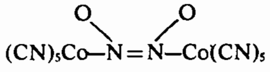
Figure 1. Infrared Spectra of $K_6[Co_2(CN)_{10}N_2O_2]$ aq (a) and $K_3[Co(CN)_6]$ (b).

The bands of the $[N_2O_2]^{2-}$ ion were assigned on the basis of the infra-red spectra of hyponitrite ion.[19-23] The hyponitrite ion has one or three bands over the range from 800-1350 cm^{-1}, depending on its cis or trans configuration. The *trans*-$[N_2O_2]$ group exhibits a single band at about 1050 cm^{-1} which results from ν_{as} (NO) vibrations; the other vibrations in this region are Raman active and are not observed in the infra-red. On the other hand, the *cis* configuration activates all three stretching vibrations ν_s (NO), ν_{as} (NO), and ν (NN) which absorb in the regions 850-1020, 1042-1115, 1300-1385 cm^{-1}, respectively. For are given in Table II with the frequencies observed by us for the cobalt complex.
comparison, the results for simple hyponitrite salts

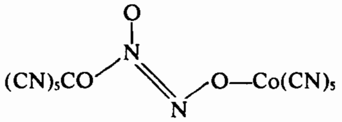
The differences in ν_{as} (NO) and ν_s (NO) frequencies between the *trans*[20] and *cis*-hyponitrites sodium and potassium[19-23]) and the bridging hyponitrite group result from the coordination effects of the ion. The presence of three bands over the region where the $[N_2O_2]$ group absorbs is an evidence of *cis* (B) or skew (C) configuration of $[N_2O_2]^{2-}$ ion in the solid complex (see below)


$(CN)_5Co{-}\underset{\underset{O}{|}}{N}{=}\overset{\overset{O}{|}}{N}{-}Co(CN)_5$

[A] *trans*



[B] *cis*



[C] skew

The bands observed below 800 cm^{-1} are consistent with those anticipated for ν(CoN), ν(CoC) δ(CoCN) vibrations and for the $[N_2O_2]$ bridging group. The infra-red spectrum of $K_3[Co(CN)_6]$ (Table I, Fig. 1) was very helpful in establishing the band assignments. The weak bands at 537, 450 and 281 cm^{-1} were assigned on the basis of theoretical vibrational analysis performed by Hisatsune and McGraw[22] for the $[N_2O_2]^{2-}$ ion. The band at 537 cm^{-1} was therefore assigned to out-of plane bonding of the ONNO group; one cannot also exclude a possibility that band at 450 cm^{-1} results from the ν(CoO) frequency which is very probable in view of the X-ray structural studies on the red nitrosyl penta-aminocobalt(III) cation performed by Hoskins et al.[24] (see skew configuration above). The band at 281 cm^{-1} may result from bending δ(NCoC) or δ(CoNO) vibrations. The other bands of this range may result from ν(CoC) and δ(CoCN) vibrations and are also observed in the spectrum of $K_3[Co(CN)_6]$ (Table I).

The spectrum of the solid complex $K_6[Co_2(CN)_{10}(N_2O_2)]$ exhibits six or seven bands over the ν(CN) frequency range 2000-2200 cm^{-1} which result from stretching vibration of the CN group whereas potassium hexacyanocobaltate has only two or three bands in this region. This splitting results most certainly from lowering of symmetry of the nitrosyl-complex in comparison with the « octahedral » $[Co(CN_6]^{-3}$ anion, and simultaneously from a strong trans-interaction of the bridging hyponitrite group as confirmed by the radioisotopic exchange studies.[18] The observed shifts and splitting also almost certainly arise from solid-state effects.

The difficulties ecountered in the interpretation of the results of studies on the kinetics of radiolysis[25]

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and polarography[26] of the aqueous solutions containing cobalt complexes encouraged us to reexamine more extensively the infra-red and electronic spectra of those solutions. The IR spectra obtained here are given in Fig. 2 and Table III.

Table III.

Spectrum of the complex in H_2O	Spectrum of the complex in D_2O	Spectrum of the complex in H_2O+D_2O	Assignment
	2160 sh,w	2180 sh,w	
	2130 vs	2125 vs	ν(CN)
2133 vs	2100 sh,w	2080 sh,m	
2092 sh,w		2045 m	
2055 sh,m		1850 m	
1820 m	1854 m	1770 w,sh	ν(NO)
1390 s	1391 s	1388 s	ν(NN)
1327 m	1330 m,sh	1327 m	
1010 w	1008 m	1015 m	ν_{as}(NO)

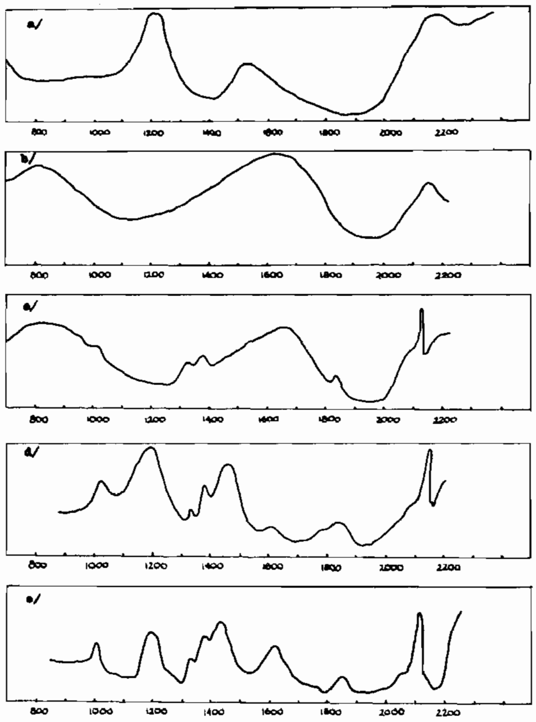

Figure 2. Infrared spectra of (a)-D_2O, (b)-H_2O, (c)-complex in H_2O, (d)-complex in D_2O, (c)-complex in $H_2O+D_2O=1:1$

On the basis of examination of infra-red spectra (Table III) one might assume the existence of an equilibrium between both dimeric and monomeric nitrosylcyanate cobalt complexes. This is manifested by the presence of bands resulting from CN and bridging N_2O_2 groups as well as some new weak bands appearing only in solutions over the range 1750-1870 cm^{-1} which are assigned to the stretching ν(NO) vibrations. The occurrence range of ν(NO) frequencies for cobalt compounds with mixture ligands reported by Lewis[13] and Feltham[27] *et al.* agrees with our observations. This equilibrium may be most probably presented as;

$$[Co_2(CN)_{10}N_2O_2]^{6-}+HOH \rightleftharpoons a[Co(CN)_5NO]^{3-}+ b[Co(CN)_5NOH]^{2-}+OH^-$$

[pH=8, a+b=2]

The presence of monomeric anions is indicated by the ν(NO) band near 1850 cm^{-1}. This suggestion has been confirmed by the results of polarographic studies.[26]

Electronic spectra

The electronic absorption of aqueous solutions and the diffuse reflectance spectra of solid complex obtained in present studies are given in Table IV. Assignments of the bands in Table IV to the corresponding electronic transitions was done on the basis of the literature data.[28-30]

Spectra of the aqueous solutions, apart from the bands expected for a D_{4h} symmetry, exhibit also the bands identical with those of a binuclear compound in the solid state. This fact confirms a monomer-dimer equilibrium existing in solution at high concentrations which has been found by the IR spectroscopic methods. Meanwhile, the number (three) and positions of bands observed in the spectrum of solution at low concentrations of the complex (Table IV) are consistent with those expected for the $[Co(CN)_5X]^{n-}$ monomers of C_{4v}, D_{4h} or D_4 symmetries[30]

Magnetic properties

The measurements, both in the solid phase and in aqueous solutions, indicate that magnetic susceptibility of the complex is about $\chi_g=-0.5 \times 10^{-6}$ and the complex is diamagnetic

Summary

On the basis of the above presented studies and discussion the final conclusion may be drawn, that in the solid state pentacyanonitrosylcobaltate(III) appears only in a polymerized form, giving the $[Co_2(CN)_{10}N_2O_2]^{6-}$ anion with a bridging hyponitrite group. In solutions, however, owing to the dissociation, the monomeric $[Co(CN)_5NO]^{3-}$ anion is also likely to appear.

General remarks: ν(NO) vibrations absorb over the range 1500-2300 cm^{-1} [31]. Even slight shifts of the electron cloud with respect to the metal or nitrogen during coordination of this group are certainly ef-

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Table IV.

Compound	Type of spectrum	Symmetry	Position of band	Assignment	Ref.
$[Co(H_2O)_6]^{3+}$	Abs.	O_h	8000 12500 16500 24700	$^1A_{1g}\rightarrow{}^3T_{1g}$ $^1A_{1g}\rightarrow{}^3T_{2g}$ $^1A_{1g}\rightarrow{}^1T_{1g}$ $^1A_{1g}\rightarrow{}^1T_{2g}$	28
$[Co(CN)_6]^{3-}$	Abs.	O_h	32400 39000	$^1A_{1g}\rightarrow{}^1T_{1g}$ $^1A_{1g}\rightarrow{}^1T_{2g}$	29
Complex in solid state	Reflex	D_{4h} or D_4	17300 24000 30600	$^1A_{1g}\rightarrow{}^1E_g$ or $^1A_1\rightarrow{}^1E(^1T_{2g})$ $^1A_{1g}\rightarrow{}^1A_{2g}$ or $^1A_1\rightarrow{}^1A_2(^1T_{1g})$ $^1A_{1g}\rightarrow{}^1E_g$ or $^1A_1\rightarrow{}^1E(^1T_{1g})$	present work
Complex in aqueous sol. (concentration range 0.1-0.5 moles/l)	Abs.	D_{4h}	11250 17000 20000sh 28000 35150 43830sh 49150	$^1A_{1g}\rightarrow{}^3A_{2g}(^3T_{1g})$ $^1A_{1g}\rightarrow{}^1E_g(^3T_{1g})$ $^1A_{1g}\rightarrow{}^1A_{2g}(^1T_{1g})$ $^1A_{1g}\rightarrow{}^1E_g(^1T_{2g})$ $^1A_{1g}\rightarrow{}^1B_{2g}(^1T_{2g})$ charge transfer C.T. $^1A_{1g}\rightarrow{}^1T_{1u}(\pi\rightarrow\pi^*)$	present work
Complex in aqueous sol. (concentr. range 10^{-1}-10^{-2} moles/l)	Abs.	D_{4h}	22700sh 26400 30800 40000 49000	$^1A_{1g}\rightarrow{}^1E_g(^1T_{1g})$ $^1A_{1g}\rightarrow{}^1A_{1g}(^1T_{1g})$ $^1A_{1g}\rightarrow{}^1E_g(^1T_{2g})$ C.T. $^1A_{1g}\rightarrow{}^1T_{1u}(\pi\rightarrow\pi^*)$	18

fected by the donor-acceptor properties of the metal, but, to some extent, are also affected by the outer sphere, solvent and other surrounding ions. Interaction with solvent may result in considerable charge shifts as is evidenced, for instance, by large differences in the ν(NO) frequencies in solid and in acetonitrile solutions, found by Cleare and Griffith.[32] The effect of solvent was found by us in the infra-red spectrum of sodium nitroprusside $Na_2[Fe(CN)_5NO]$ (ν(NO) = 1939 cm^{-1}) dissolved in heavy water (1926), metryl alcohol (1900), acetic acid (1922), dioxane (1936), D_2O+HCl mixture (1930) and D_2O+NaOH mixture (1930 cm^{-1}). Slight differences in frequencies of ν(NO) vibrations result from the polarity of the medium which affects the shift of the charge between ligand and metal. The ease of polarisation inside of the NO–group causes the N–O bond to absorb the infra-red radiation in such a wide range of energy. Only the ν(NO) frequencies of the bridging $[N_2O_2]$ group, for which the nitrogen-oxygen bond order is about 1, differ considerably from those mentioned above.

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