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# Spectroscopy and Magnetic Properties of Nitrosylpentaamminechromium Salts

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Nitrosylpentaamminechromium chloride (brown), perchlorate (green) and other salts of different colors were studied by visible, IR and ESR spectroscopy and by magnetic susceptibility measurements. The easy shift of visible absorption bands caused by the replacement of outer anions which are responsible for the color difference, ripples observed in one of the absorption bands, *g*-values from ESR and a spin state 1/2 suggested by the susceptibility measurements are interpreted on the basis of a qualitative MO theory for metal nitrosyl complexes.

A series of transition metal nitrosyl compounds $[MNOL_5]X_n$[1] are known, where M is Fe, Mn, Co, Cr or Pt, L is CN, $NH_3$ or $H_2O$ and X is Cl, Br, $NO_3$ or $ClO_4$, *etc.* These compounds are known to be quite peculiar, both from phenomenological and theoretical view points. Most of these compounds have very short M–N distances, for example, 1.63 Å in $[Fe(CN)_5NO]^{2-}$,[2] which

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[1] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, **1959**, 872; W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, **1961**, 775; M. Ardon and J. I. Herman, *ibid.*, **1962**, 507; W. P. Griffith, *ibid.*, **1963**, 3286.

[2] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

shows the existence of $\pi$-bonding between M and NO resulting in a strong ligand field around the metal ion. This is confirmed by magnetic measurements, which indicate low spin.

Gray and Ballhausen[3] considered that such a short distance should result in a strong axial destabilization of d orbitals, and gave an orbital energy level scheme for $M(CN)_5NO$ ion based on crystalline field theory. Gray and Bernal[4] treated the same problem by molecular orbital theory, where they considered the formation of strong $\pi$-bonds involving the metal $nd_{xz}$ and $nd_{yz}$ orbitals and the nitrosyl $\pi^*(2p_x, 2p_y)$ antibonding orbitals. Recently, a more detailed molecular orbital calculation has been made by Gray, Manoharan, Pearlman and Riley[5] and Manoharan and Gray.[6] Their results suggest that the energy level derived mainly from the nitrosyl antibonding orbital $\pi^*$ NO (which corresponds to the 4e level of Fig. 4), lies much lower than previously suspected.

Extensive optical spectroscopy[3,6,7] and ESR experiments[8] were carried out on transition metal nitrosyl complexes, especially on $[Fe(CN)_5NO]^{3-}$, $[Cr(CN)_5NO]^{3-}$, $[CrNO(NH_3)_5]^{2+}$ and $[CrNO(H_2O)_5]^{2+}$ ions. Infrared absorptions[9,10] of nitrosyl ligands in these compounds were also well investigated.

It is known that $[CoNO(NH_3)_5]^{2+}$ salts have two isomeric forms, one being the red series and the other the black series. From the rocking frequencies[11] of ammonia ligands in these compounds, it was inferred that the oxidation state of Co ion is three in both the red and black series. The electric conductivity[12] of solutions of these complexes showed that the red series of $CoNO(NH_3)_5$ salts are dimers and the black ones monomers, the latter result being consistent with X-ray data.[13]

Nitrosylpentaamminechromium salts,[14] which are subjects of the present study, also have several characteristic properties. Their color is a function of the outer anions present in the solid state. This suggests considerable effects of outer anions on the ligand field at the metal ion (*cf.* Fig. 1). Thus, solid nitrosylpentaamminechromium chloride, bromide and nitrate are brown, while perchlorate,

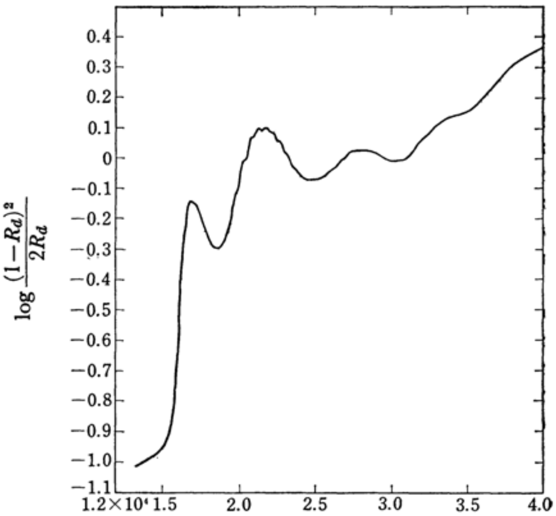

Fig. 1. (a)

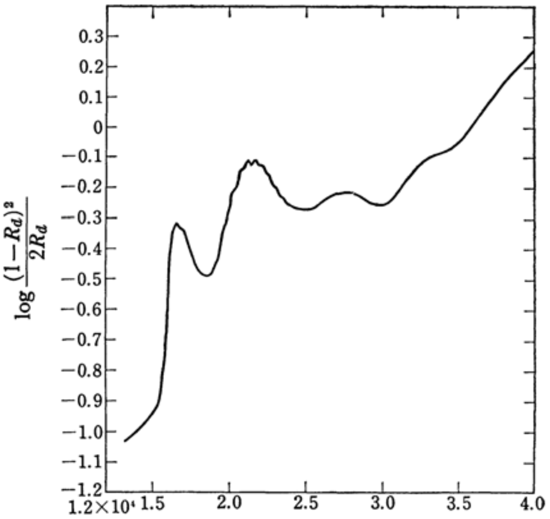

Fig. 1. (b)

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[3] H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, **36**, 1151 (1962).

[4] H. B. Gray, I. Bernal and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962).

[5] H. B. Gray, P. T. Manoharan, J. Pearlman and R. F. Riley, *Chem. Commun.*, **1965**, 62.

[6] P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).

[7] B. A. Goodman, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc.*, (*A*), **1966**, 994.

[8] F. A. Cotton, R. R. Monchamp, R. J. M. Henry and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959); I. Bernal and S. E. Harrison, *J. Chem. Phys.*, **34**, 102 (1961); J. J. Fortman and R. G. Hayes, *ibid.*, **43**, 15 (1965); I. Bernal, S. D. Robinson, L. S. Meriwether and G. Wilkinson, *Chem. Commun.*, **1965**, 571; J. Danon, H. Panepucci and A. A. Misetich, *J. Chem. Phys.*, **44**, 4154 (1966); J. Danon, R. P. A. Muniz and A. O. Cariae, *ibid.*, **46**, 1210 (1967).

[9] J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

[10] W. P. Griffith, J. Lewis and G. Wilkinson, *ibid.*, **7**, 38 (1958).

[11] E. P. Bertin, S. Mizushima, T. J. Lane and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3821 (1959).

[12] R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964).

[13] D. Hall and A. A. Taggart, *J. Chem. Soc.*, **1965**, 1359; D. Dale and D. C. Hodgkin, *ibid.*, **1965**, 1364.

[14] M. Mori, S. Ueshiba and S. Kawaguchi, This Bulletin, **36**, 796 (1963); W. P. Griffith, *J. Chem. Soc.*, **1963**, 3286.

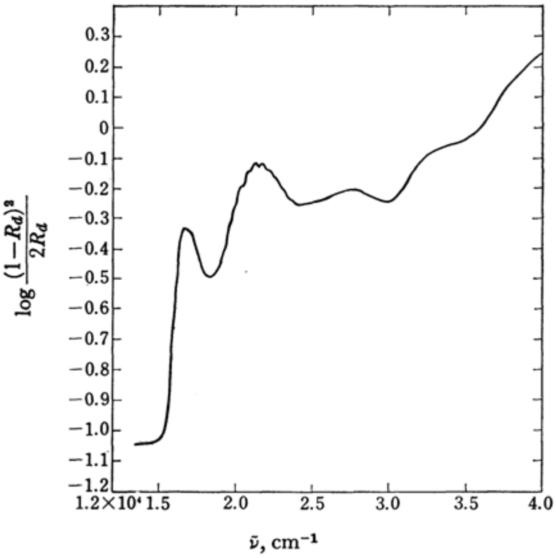

Fig. 1. (c)

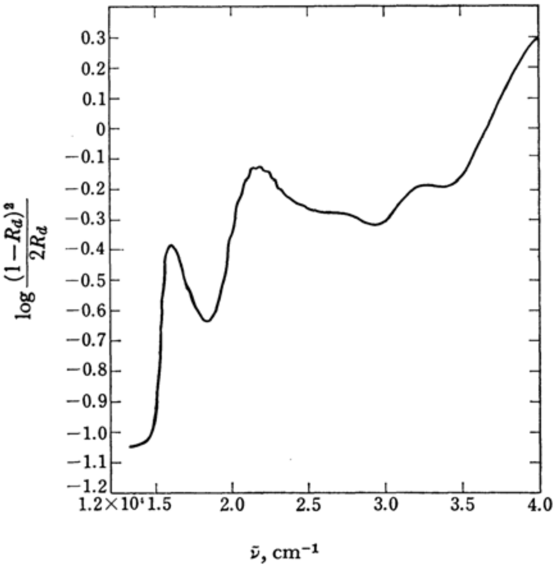

Fig. 1. (d)

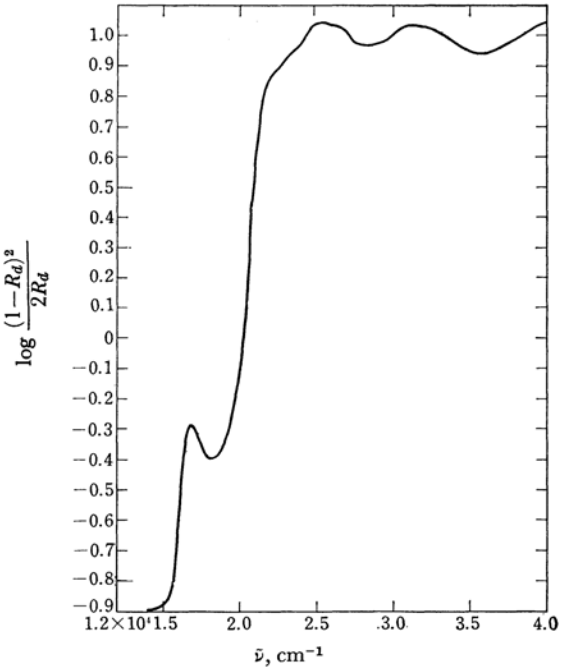

Fig. 1. (e)

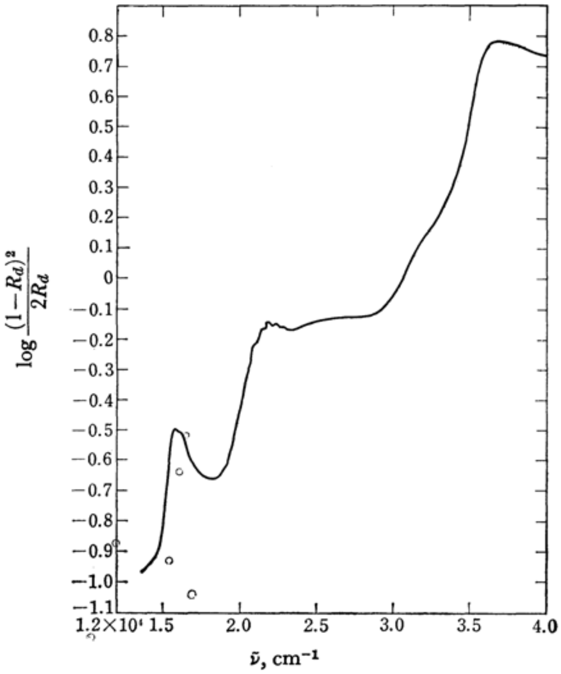

Fig. 1. (f)

Fig. 1. Absorptions found in reflection spectra.

(a): $[CrNO(NH_3)_5]Cl_2$
(b): $[CrNO(NH_3)_5]Br_2$
(c): $[CrNO(NH_3)_5](NO_3)_2$
(d): $[CrNO(NH_3)_5](ClO_4)_2$
(e): $[CrNO(NH_3)_5][B(C_6H_5)_4]_2$
(f): $[CrNO(NH_3)_5][OC_6H_2(NO_2)_3]_2$

tetraphenylborate and picrate are green. The absorption bands of nitrosylpentaamminechromium salts in the visible region have ripples which occur at equal intervals.[15] The salts also are in low spin states even though they are one type of pentaamminechromium salt. The present paper deals

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[15] M. Mori, Preprints for the 16th Annual Meeting of the Chemical Society of Japan (1963, Tokyo); I. Bernal, S. D. Robinson, L. S. Meriwether and G. Wilkinson, *Chem. Commun.*, **1965**, 571.

with studies of visible reflection, visible absorption, infrared and ESR spectra and of the magnetic susceptibilities of nitrosylpentaamminechromium salts.

## Experimental

The nitrosylpentaamminechromium salts were prepared by the method reported by Mori, Ueshiba and Kawaguchi.[14] In this paper, previously unreported tetraphenylborate and the picrate of this complex were prepared by adding the corresponding sodium salt or free acid to aqueous solutions of the chloride.

Found in nitrosylpentaamminechromium picrate: Cr, 8.16; $NH_3$, 12.80%. Calcd for $[CrNO(NH_3)_5](C_6H_2N_3O_7)_2$: Cr, 8.32; $NH_3$, 13.58%. Found in nitrosylpentaamminechromium tetraphenylborate: C, 71.69; H, 6.76; N, 9.58%. Calcd for $[CrNO(NH_3)_5][B(C_6H_5)_4]_2$: C, 71.7; H, 6.88; N, 10.44%.

Hexaamminechromium(II) perchlorate was prepared by mixing chromium(II) acetate (prepared from 5 g of potassium dichromate[16]) with 15 g of ammonium perchlorate and 75 m*l*, of 15 M aqueous ammonia in the absence of atmospheric oxygen. The blue precipitate formed was centrifuged or filtered and washed, first with an ammonical aqueous solution of ammonium perchlorate, then with ethanol and finally with petroleum ether. The compound readily oxidizes in air, so that weighing the sample is difficult. However, the atomic ratio was determined to be Cr : $NH_3$ : $ClO_4$=1 : 6.10 : 1.97 in a mixed solution prepared by adding the sample wet with petroleum ether to dilute hydrochloric acid. At the same time, the precipitate was shown to be isomorphous with $[M(NH_3)_6](ClO_4)_2$ (M=Mn, Fe, Co, Ni) by an X-ray powder technique. It is thus clear that the blue compound was $[Cr(NH_3)_6](ClO_4)_2$. For the IR study, the mother liquor was further replaced with liquid paraffine. In this liquid, the compound was comparatively stable even between the two plates of sodium chloride used for IR spectroscopy.

The reflection spectra of these complex compounds in powder were obtained using a Hitachi Perkin-Elmer 139 UV-VIS Spectrophotometer. In Fig. 1, such spectra are expressed in terms of $\log[(1-R_d)^2/2R_d]$, where $R_d$ is the diffuse reflectance. This type of curve more clearly shows the relation to absorption spectra. The positions of main maxima in such curves for various

TABLE 1. ABSORPTION MAXIMA FOUND IN REFLECTION SPECTRA OF $[CrNO(NH_3)_5]X_2$

| X | Absorption maxima ($cm^{-1}$) | | | | |
|---|---|---|---|---|---|
| Cl | 16850<br>17200(sh) | 21700 | 27800 | 33300 | |
| Br | 16600<br>17000(sh) | 21700 | 27700 | 33300 | 39500 |
| $NO_3$ | 16600<br>17000(sh) | 21700 | 27500 | 33000 | |
| $ClO_4$ | 15900<br>16300(sh) | 21800 | 26700 | 32500 | 40000 |
| $B(C_6H_5)_4$ | 15700<br>16300(sh) | 21900 | 27000 | 32300(sh) | 37000<br>$(B(C_6H_5)_4)$ |
| $OC_6H_2-(NO_2)_2$ | 16800<br>17300(sh) | ? | | | |

TABLE 2. INFRARED ABSORPTION MAXIMA OF $[CrNO(NH_3)_5]X_2$

| Mode of Vibration | $[CrNO(NH_3)_5]X_2$, X= | | | | | |
|---|---|---|---|---|---|---|
| | Cl | Br | $NO_3$ | $ClO_4$ | $B(C_6H_5)_4$ | $OC_6H_2-(NO_2)_3$ |
| Cr↔$NH_3$ stretch. | 440 m | | | 420 m | | |
| Cr–NO bend. | 534 vw* | | | 531 w* | | |
| Cr↔NO stretch. | 572 w* | | | 575 vw* | | |
| N–O stretch. | 1680 vs | 1690 vs | 1670 vs | 1730 vs | 1730 | 1715 |
| $ClO_4$ | | | | 463 vw<br>457 vw | | |
| $NH_3$ rock. | 770 s(B)<br>730 sh | 760 s<br>730 sh | 770 s<br>730 sh | 730 s<br>760 sh | ? | ? |
| $NH_3$ sym. deform. | 1275 vs(S) | 1280 vs | 1286 vs | 1300 vs(S) | 1300 vs | ? |
| $NH_3$ stretch. | 3300 vs(B) | | | 3410 vs(S)<br>3340 vs(S) | | |
| $NH_3$ stretch. | 2960 vs(S)<br>2900 vs(S) | | | 2960 vs(S)<br>2900 vs(S) | | |
| $NH_3$ deg. deform. | 1610 s | | | 1625 s | | |

* Assignment by Miki, Ishimori, Yamatera and Okuno.[18]

s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, S: sharp, B: broad, ?: values could not be determined.

TABLE 3. *g*-VALUES OBTAINED BY ESR FOR $[CrNO(NH_3)_5]X_2$ IN POWDER AND IN AQUEOUS SOLUTION

| X | *g*-Values | | |
|---|---|---|---|
| | Powder r. t. | Solution r. t. | Solution liq. $N_2$ temperature |
| Cl | 1.989 | 1.979 | |
| Br | 1.985 | —— | |
| $NO_3$ | 1.986 | 1.979 | |
| $ClO_4$ | 1.982 | 1.980 | |
| $B(C_6H_5)_4$ | $1.945(g_{//})$<br>$2.006(g_{\perp})$ | $1.975^{\times}$ | $1.943(g_{//})^{\times}$<br>$2.004(g_{\perp})^{\times}$ |
| $OC_6H_2(NO_2)_3$ | 1.968 | $1.976^{\times}$ | $1.946(g_{//})^{\times}$<br>$2.005(g_{\perp})^{\times}$ |

r. t.: at room temperature,

×: solution in acetone, others are in aqueous, solutions.

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[16] S. M. Jörgensen, *J. prakt. Chem.*, **30**, 6( 1884); "Inorganic Syntheses," Vol. 1, p. 122 (1939); Vol. 3, p. 148 (1950); Vol. 6, p. 145 (1960) and Vol. 8, p. 125 (1966), McGraw-Hill Book Company, Inc., New York and London.

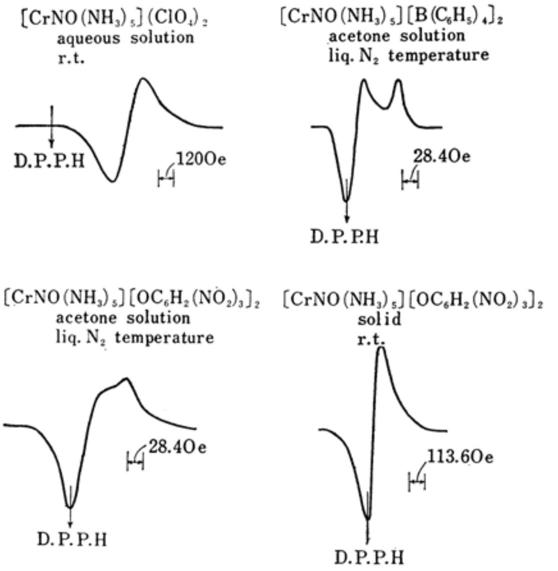

Fig. 2. ESR spectra.

compounds are given in Table 1. The absorption spectra in the visible region of these complex compounds in aqueous solutions were obtained using a Hitachi EPS-2 Recording Spectrometer. In aqueous solutions all compounds showed spectra indistinguishable from each other, irrespective of outer anions.

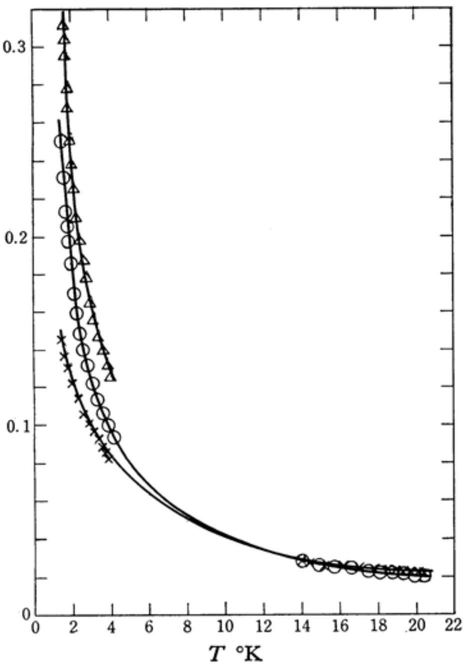

Fig. 3. The molar magnetic susceptibilities (C.G.S. E.M.U.) in powder.

×: $[CrNO(NH_3)_5]Cl_2$, △: $[CrNO(NH_3)_5](NO_3)_2$, ○: $[CrNO(NH_3)_5](ClO_4)_2$

Table 4. The results of the measurements between 1.2°K and 20°K of the magnetic susceptibilities of $[CrNO(NH_3)_5]X_2$ salts

| X | Effective Bohr magneton no. | Curie-Weiss const. |
|---|---|---|
| Cl | 1.9 | −1.5°K |
| Br | 2.0 | −1.2°K |
| $NO_3$ | 2.0 | −0.19°K |
| $ClO_4$ | 1.8 | −0.10°K |
| $B(C_6H_5)_4$ | 1.6 | −0.080°K |

Infrared absorptions of nitrosylpentaamminechromium salts were observed using a Hitachi EPI infrared Spectrometer. The numerical results are listed in Table 2.

Electron spin resonance spectra were obtained on a Tokyo Denki Seiki T-1000 AX ESR Spectrometer. The results are given in Table 3 and shown in Fig. 2.

The magnetic susceptibilities in the temperature region 1.2°K to 20°K were observed by an alternating current method using a Hartshorn Bridge. The accuracy was ±0.1%. The susceptibilities obeyed the Curie-Weiss law (Fig. 3) and the effective magnetic moments and Curie-Weiss constants were obtained as given in Table 4.

## Discussion

The magnetic moments obtained at low temperatures (Table 4) indicate that both brown and green salts are in the same spin state of 1/2, and are in agreement with the room temperature data (2.3 Bohr magnetons) reported for the chloride by Griffith.[1] The fact that the susceptibilities obey the Curie-Weiss law down to 1.2°K proves that no dimerization occurs, and in this sense both brown and green salts correspond to the black series of nitrosylpentaamminecobalt salts. However, the Curie-Weiss constants of the brown halides are greater than those of the green salts, suggesting a greater interaction of spins in the former, presumably through anions. As seen from numerical data in Tables 1—4, the various properties, as well as the colors of these chromium complexes, change continuously rather than abruptly from complex to complex. Consequently, such differences in properties, although considerable in some cases, are thought to be due only to a change in the degree of an interaction between the complex cation and the outer anion.

The rocking frequency of ligand ammonia is known to be sensitive to the oxidation state of the central metal ion. The rocking frequency of ammonia ligands in hexaamminechromium(III) perchlorate is 718 cm$^{-1}$, and that in hexaamminechromium(II) perchlorate, which we newly prepared, was found at 660 cm$^{-1}$. The rocking frequencies in the nitrosylpentaamminechromium salts (730—770 cm$^{-1}$, Table 2) fall within the range for Cr(III) complexes, and are considerably higher than that of the Cr(II) complex. Furthermore, the stability in water of our nitrosylpentaamminechromium complexes is comparable to that of Cr(III) ammine complexes. These results may appear to contradict the magnetic data, because the spin state of 1/2 suggests monovalent Cr. However, we note that the same spin state of 1/2 is reached either when we start with monovalent Cr($3d^5$) and a $NO^+$ ligand by considering extensive back donation, or when we start with trivalent Cr($3d^3$) and $NO^-$ ligand and consider electron pairing. In any interpretation, the result is the formation of a strong $\pi$-bond between Cr and NO as proposed by many investigators, and the concept of oxidation state seems to lose its strict meaning in harmony with Orgel's view.[17] The anomalous bond strength between chromium and nitrosyl is also supported by the fact that the nitrosylpentaamminechromium salts are changed into pentacyanonitrosylchromium salts in KCN solutions without inducing cleavage of the chromium-nitrosyl bond. In this respect, molecular orbital treatment seems to be suitable for a theoretical consideration of the orbital energy levels of these complexes. Manoharan and Gray[6] made a molecular orbital calculation using $[Fe(CN)_5NO]^{2-}$ as the model ion, and the essential features should remain unchanged for $[CrNO(NH_3)_5]^{2+}$ ion. Thus, the general idea of the energy level scheme of the latter ion could be illustrated as in Fig. 4. Here we assume linearity and the arrangement order Cr–N–O, which seem probable from the recent IR study by Miki *et al.*[18]

Clear-cut assignments of the observed absorption spectra seem difficult, but some characteristics of the absorption bands can be treated as follows:

Reflection spectra in powders indicate that the color changes of the above solid complexes are due to a shift of the visible absorption band in the range 16000—17000 cm$^{-1}$ ($\varepsilon$=18.2 in aqueous spectrum). The easy shift of this band can be interpreted by assigning it to a one-electron transition $1b_2(3d_{xy})\rightarrow 4e(\pi^*NO, 3d_{xz}, 3d_{yz})$ (*i. e.*, $B\rightarrow{}_2E$). The excited orbital 4e is a $\pi$-type antibonding molecular orbital located mainly on the nitrosyl, and should be easily influenced by an anion. The direction of shift of the absorption band agrees with this assumption, because the chloride ion which is thought to behave as an electron donor and thus raises the $\pi^*$NO level by interaction, actually causes the band to shift toward shorter wavelengths.

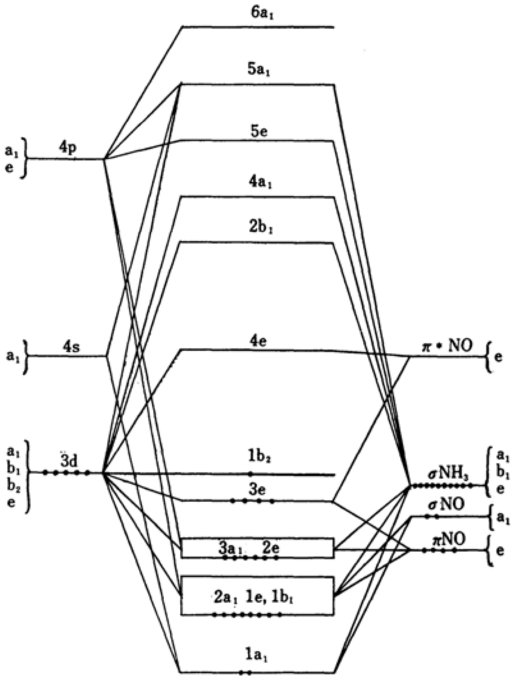

Fig. 4. Molecular orbital energy level for $[CrNO(NH_3)_5]^{2+}$.

The powder spectra also show that the above band is composed of two closely spaced peaks, one of which appears as a shoulder (Fig. 1 and Table 1). This may either be due to a splitting of the 4e level by crystal anisotropy or to the superposition of another band, $3e(3d_{xz}, 3d_{yz})\rightarrow 4e(\pi^*NO, 3d_{xz}, 3d_{yz})$ (*i. e.*, $B_2\rightarrow B_2+B_1+A_2+A_1$).

The absorption band near 22000 cm$^{-1}$ ($\varepsilon$=101 in aqueous spectra) is accompanied by ripples spaced at about 480—490 cm$^{-1}$ intervals in aqueous as well as in powder reflection spectra, as shown in Fig. 1, a—f. The wave numbers of small peaks or shoulders in such ripple structures and their spacings are given in Table 5. It seems most probable that the ripple is caused by the coupling of vibrations with the electric dipole transition. We note that vibrational structures on absorption bands have never been reported in other ammine complexes, even when such bands are thought to be allowed only through coupling with vibrational modes. We are thus inclined to think that in this nitrosyl ammine complex there is a special situation in addition to such coupling which made the vibrational structure perceptible in actual spectra. We attribute this to the vibrational stability in the excited state brought about by metal-nitrosyl double bonding, in the sense that there is a well-defined potential minimum even in the excited electronic state. We shall now give some interpretation of a more detailed nature on the problem on these lines.

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[17] L. E. Orgel, "An Introduction to Transition-Metal Chemistry, Ligand-Field Theory," Methuen and Co. Ltd., London, John Wiley and Sons Inc., New York (1960), pp. 37, 145.

[18] E. Miki, T. Ishimori, H. Yamatera and H. Okuno, Proceedings of the Tenth International Conference on Coordination Chemistry, 141 (1967) Tokyo and Nikko, Japan; E. Miki, This Bulletin, **41**, 1835 (1968).

TABLE 5. WAVE NUMBERS AT SMALL PEAKS OR SHOULDERS IN THE RIPPLE STRUCTURE OF 22000 $cm^{-1}$ BAND

| | | | | | $[CrNO(NH_3)_5]X_2$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| X=Cl | | Br | | $NO_3$ | | $ClO_4$ | | $B(C_6H_5)_4$ | | aq. soln. | |
| $cm^{-1}$ | $\Delta$ | $cm^{-1}$ | $\Delta$ | $cm^{-1}$ | $\Delta$ | $cm^{-1}$ | $\Delta$ | $cm^{-1}$ | $\Delta$ | $cm^{-1}$ | $\Delta$ |
| 23630 | | 23520 | | 23540 | | 23760 | | 23800 | | 23400 | |
| | 470 | | 420 | | 420 | | 540 | | 510 | | 480 |
| 23160 | | 23100 | | 23120 | | 23220 | | 23290 | | 22920 | |
| | 460 | | 480 | | 450 | | 430 | | 410 | | 490 |
| 22700 | | 22620 | | 22670 | | 22790 | | 22880 | | 22430 | |
| | 460 | | 440 | | 490 | | 470 | | 530 | | 550 |
| 22240 | | 22180 | | 22180 | | 22320 | | 22350 | | 21880 | |
| | 540 | | 510 | | 470 | | 490 | | 470 | | 470 |
| 21700 | | 21670 | | 21710 | | 21830 | | 21880 | | 21410 | |
| | 470 | | 470 | | 500 | | 470 | | 480 | | 430 |
| 21230 | | 21200 | | 21210 | | 21360 | | 21400 | | 20980 | |
| | 480 | | 500 | | 510 | | 460 | | 440 | | 500 |
| 20750 | | 20700 | | 20700 | | 20900 | | 20960 | | 20480 | |
| | 430 | | 480 | | 490 | | 530 | | 440 | | 510 |
| 20320 | | 20220 | | 20210 | | 20370 | | 20420 | | 19970 | |
| | 590 | | 520 | | 510 | | 480 | | 510 | | |
| 19730 | | 19700 | | 19700 | | 19890 | | 19910 | | | |
| | 510 | | | | | | 560 | | | | |
| 19220 | | | | | | 19330 | | | | | |
| mean | 490 | | 478 | | 480 | | 492 | | 486 | | 490 |

The band with ripples under discussion (22000 $cm^{-1}$) is one which undergoes the least change in wave numbers with the substitution of outer anions. This fact, as well as the energy value, suggests the assignment $1b_2(3d_{xy}) \to 2b_1(3d_{x^2-y^2})$, $(B_2 \to B_1)$ for this band. This transition must couple with a vibration of E symmetry in order to be allowed. Vibrations of E symmetry observed in IR spectra in the neighborhood of 500 $cm^{-1}$ are a bending vibration of the CrNO skeleton as observed by Miki *et al.*[18] at 531—535 $cm^{-1}$, and a $Cr–NH_3$ stretching vibration as observed at 420—440 $cm^{-1}$ by the present authors (Table 2). Although Bernal cited the possibility that the ripple structure on the 22000 $cm^{-1}$ absorption band is due to coupling of the latter vibration, it is felt even more probable to the present authors that it should be due to coupling with the Cr–N–O bending vibration, since the vibrational frequencies are expected to decrease in the excited level. Furthermore, if it were attributable to the $Cr–NH_3$ E stretching mode as in Bernal's assumption, the ripple structure should appear in other ammine complexes as well, which is not the case. Furthermore, our assumption does not contradict the fact that the excitation $B_2 \to B_1$ does not break the Cr–N–O linkage.

Other absorption bands, *i. e.*, at 28000 $cm^{-1}$ and 33000 $cm^{-1}$ observed for the perchlorate, also shift toward the violet region by about 1000 $cm^{-1}$ upon substituting the outer anions with halide ions. They probably include transitions $3e(3d_{xz},3d_{zy}) \to 4a_1(3d_{z^2})(B_2 \to E)$, $1b_2(3d_{xy}) \to 4a_1(3d_{z^2})(B_2 \to A_1)$, *etc.*

The ESR results on nitrosylpentaamminechromium complexes in solution agrees with the results of Bernal and Harrison[8] and Danon, Panepucci and Misetich.[8] Though the nitrosylpentaamminechromium salts could not be obtained as single crystals, powder spectra of tetraphenylborate and of picrate at liquid $N_2$ temperature gave structures typical of an anisotropic $g$-tensor, and $g_\perp$ and $g_{//}$ were estimated using Kneubühl's method.[19] The situation seems analogous to the case of dimelammonium hexachlorocuprate,[20] which also has a large organic ion exhibiting a dilution effect, enabling one to observe an anisotropic fine structure. The spin-orbit interaction constant calculated from the $g_{//}$ obtained using the energy gap $E(B_{1g}-B_{2g})=22000$ $cm^{-1}$ is $\zeta=158$ $cm^{-1}$.

## Conclusion

Nitrosylpentaamminechromium salts, both the brown and green series, are in low spin states (1/2) and are thus thought to be monomers. The easy shift of the absorption band in the range 16000—17000 $cm^{-1}$, observed as color differences in powders, is attributable to a rise in energy of the excited level $\pi^*NO$ cused by a donor-acceptor interaction with anion acting as a donor. Ripples having intervals of about 500 $cm^{-1}$, observed on the absorption bands near 22000 $cm^{-1}$, are presumably the result of coupling of vibrational frequencies of the Cr–N–O bending mode (E) with the electric dipole transition $B_1 \to B_2$.

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