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The Position of 2,2'-Bipyridine and 1,10-Phenanthroline in the Spectrochemical Series

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Dedicated to Professor K. A. Jensen on his 70th birthday

New mixed-ligand complex ions $[M(III)(NH_3)_{6-2a}(N\text{-}N)_a]^{3+}$ (M = Cr and Co; (N-N) = bipy and phen; $a = 1$ and 2) have been prepared in mixtures, separated chromatographically and isolated as perchlorates. Comparative ligand field spectral studies (within the expanded radial function model) of these complexes and of relevant Ni(II) complexes reported in the literature reveal, in consensus with literature, that the heteroaromatic ligands (N-N) lie above the amines in the spectrochemical series when the central ions are Co(III) and Ni(II). However, contrary to literature conclusions, the opposite relationship is found for Cr(III). Certain irregularities found between the spectra of corresponding Cr(III) and Co(III) complexes invite the conclusion that the cyanide ion as a ligand gives rise to pronouncedly more π-back-bonding when bound to Co(III) than when bound to Cr(III), and the same is found to be true for the (N-N)-ligands, but to a much lesser extent. From tris(N-N)Ni(II) complexes it appears that the (N-N)-ligands lie below ammonia in the nephelauxetic series, and they lie below ethylenediamine in the hyperchromic series when the central ions are Cr(III) or Co(III).

Various consequences of the approximately Gaussian shape of absorption bands are discussed and the empirical average environment rule is shown for $A_i \rightarrow T_j$ transitions (i and j independently taking on the values 1 or 2) of cubic complexes with small low-symmetry perturbations to be derivable under the assumptions about a pure cubic parentage of the excited level and about equal heights and widths of band components.

I. INTRODUCTION

The spectrochemical series[1] of ligands was originally purely empirical and listed the ligands X^{x-} in the order of increasing energy of the so-called first absorption band of $[Co(NH_3)_5X]^{(3-x)+}$ complexes. This band situated at about 20 000 cm^{-1} was later assigned[2,3] as the transition $^1A_{1g}(O_h) \rightarrow {}^1T_{1g}(O_h)$. The same series was obtained analogously on the basis of other complexes[4] such as $[Co\ en_2\ X_2]^{(3-2x)+}$.

The experimental results[5] further showed that the molar absorptivities ε_{max} for both the first and the second absorption band varied with X^{x-} even much more than did the energies.

This variation was the same for the above two types of complexes and on this basis a so-called *hyperchromic series*[5] was established.

When ligand field theory began to be used for the interpretation of absorption spectra, the expanded radial function model * was applied to these complexes, and it became clear that the spectrochemical series could be interpreted[3] as a series of increasing values of this model's empirical parameter Δ defined by

$$\Delta = h[e_g(O_h)] - h[t_{2g}(O_h)] \qquad (1)$$

when referring to regularly octahedral complexes. Δ was at the time[3] often called $10Dq$. When Δ is given a sub-index X^{x-}, $\Delta_{X^{x-}}$ refers

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* The expanded radial function model[6] is a symmetry-based semi-empirical model which takes empirical parameters for the ligand field as well as for the interelectronic repulsion.

to the $[CoX_6]^{(3-6x)+}$ complex. $h[\gamma(O_h)]$ of eqn. 1 is the one-electron energy of the expanded radial function model associated with the d orbital spanning the irreducible representation γ of the octahedral group O_h. This interpretation of the spectrochemical series in terms of the empirical parameter Δ made it possible to study the series also for other metal ions and such studies soon led to the discovery [7] that the series of ligands was essentially the same for all central ions for which it could be studied.

The spectrochemical properties of the ligands 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) are only known [8] with certainty for nickel(II) as the central ion. In this case the heteroaromatic ligands both lie *ca.* 12 % above ammonia and *ca.* 5 % above ethylenediamine in the Δ-series, their relative position being a little uncertain as further discussed in section V in connection with Table 3. When bound to cobalt(III) in tris-complexes bipy and phen are also above ammonia and ethylenediamine in the spectrochemical series [9–11] as will be discussed in the present paper, but for chromium(III) there is a lack of agreement on this point. Some authors [12] have assigned shoulders at 22 000 and 23 000 cm^{-1} in the complexes $[Cr\ bipy_3]^{3+}$ and $[Cr\ phen_3]^{3+}$, respectively, as the $^4A_{2g}\rightarrow{}^4T_{2g}(O_h)$ transition whose energy is a direct measure of Δ. Other authors [13] concluded that Δ for $[Cr\ bipy_3]^{3+}$ is 23400 cm^{-1} and the present authors [14] gave some indication based upon the spectra of di-μ-hydroxo complexes that both these ligands have Δ-values which are smaller than or comparable to that of ethylenediamine.

The purpose of the present paper is to further elucidate this problem. New mixed-ligand chromium(III) and cobalt(III) complexes containing ammonia and bipy or phen (the latter two ligands being designated in the following by the common symbol N-N) have been prepared and their spectra studied to provide quantitative information concerning the Δ values for these heteroaromatic ligands and thereby their positions in the spectrochemical series for chromium(III) and cobalt(III).

II. ATTEMPTS AT A CHEMICAL INTERPRETATION OF Δ

It was early realized [15] that the symmetry properties of the d-orbitals might give some understanding of the physical background for the ligand field parameter Δ of eqn. (1). Thus the e_g orbitals are able to form σ-bonds (but not π-bonds) with the ligands and the t_{2g} orbitals can form π-bonds (but not σ-bonds). In molecular orbital language Δ for most ligands could then be interpreted as the difference between a σ-antibonding and a π-antibonding action from the filled ligand orbitals on the d orbitals as expressed by the equation

$$\Delta = \Delta_\sigma - \Delta_\pi \tag{2}$$

For special ligands,[16] the so-called π-acceptor ligands, with low lying empty or only partially filled orbitals, a π-bonding action could also be present and this could then give a positive contribution to the value of Δ. These considerations are generalized in the semi-empirical angular overlap model,[17,18] which may be considered a zeroth order molecular orbital model.

With the interpretation of Δ expressed in eqn. (2) the fact that the spectrochemical series hardly depends on the central ion [7] is perhaps acceptable for ligands without π-acceptor properties and it is also acceptable that Δ increases with the oxidation state of the metal ion, as illustrated by the following d^3 examples: [19–21]

$$\begin{aligned}&\Delta([MnF_6]^{2-})/\Delta([CrF_6]^{3-}) = \\ &\quad 21\,800/15\,200 = 1.43\\ &\Delta([Cr(H_2O)_6]^{3+})/\Delta\{[V(H_2O)_6]^{2+}\} = \\ &\quad 17\,400/12\,400 = 1.40\end{aligned} \tag{3}$$

But for π-acceptor ligands the lower oxidation state would have to obtain the larger positive contribution to Δ from π-back donation (*i.e.* charge transfer from the central ion to the ligand), and therefore for such ligands irregularities in the spectrochemical series would be expected to occur at least when metal ions with the same electron configuration but different oxidation states were compared. Actually the fact that the d^6 system $[Mn(CN)_6]^{5-}$ is colourless and thus has no ligand field bands in the visible region was early taken as evidence [22] that the ligand CN$^-$ which potentially belongs to the π-acceptor class also effectively does so.

The reasoning can be represented as follows. From eqn. (3) it is seen that Δ is reduced by a factor of approximately 1.4 as the oxidation state is reduced from 4 to 3 and from 3 to 2. If one assumes the same factor of reduction on going from oxidation state 2 to 1 and if one further assumes that the same factor applies to the ratios between the wave numbers σ_1 of the first spin-allowed absorption band ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ of d^6 systems (*cf* Table 1) then it is possible on the basis of σ_1 for $[Co(CN)_6]^{3-}$ (32 200 cm^{-1}) to predict a value of 16 000 cm^{-1} for $[Mn(CN)_6]^{5-}$. The lack of colour of this complex, however, places a lower limit of 26 000 cm^{-1} on the experimental quantity σ_1, and the conclusion is that considerable π-back-bonding has taken place.

Ligand field data are scarce for π-acceptor ligands, particularly for low oxidation states of the central ion, since these often have their ligand field bands covered[10,11] by backward electron transfer bands, *e.g.* $[Fe\ phen_3]^{2+}$. Recently, however, some ligand field data for chromium(III) pyridine complexes could be interpreted using a net negative angular overlap model π-parameter[23] corresponding to weak net backward π-bonding in exactly the sense that we have discussed here.

It is interesting in this context to compare (Table 1) data for d^3 and low-spin d^6 systems, the latter of which belongs to the class of complexes which obeys the so-called noble gas rule by having the number of σ-donated electrons and the number of metal electrons adding up to the number of electrons of krypton. It is seen from Table 1 that the ratio $\Delta(Co)/\Delta(Cr)$ is fairly constant for the ligands without π-acceptor character while the Δ value for CN^- is relatively much higher for the d^6 system. This is a piece of ligand field theoretical evidence for the amusing fact that the noble gas rule, which in its formulation is only concerned with σ-electrons from the ligands, has energetic consequences only when these same ligands are also π-acceptors.

It is always tempting to try to assess how far such chemical reasoning about parameters of physical models makes sense.

In the present case one might reason as follows. Δ is not as fundamental a parameter as its constituents $\Delta\sigma$ and $\Delta\pi$ of eqn. (2). Therefore the fact that $\Delta(Co)/\Delta(Cr)$ is a constant for ligands with vanishing or small and positive $\Delta\pi$ parameter values[23] makes it likely that the following relation is approximately valid for these ligands:

$$\frac{\Delta(Co)}{\Delta(Cr)} = \frac{\Delta\sigma(Co)}{\Delta\sigma(Cr)} = \frac{\Delta\pi(Co)}{\Delta\pi(Cr)} \cong 1.05;\ C=4B \qquad (4)$$

Table 1. Values of the wavenumbers[33] (in kK units) of the maxima of the first spin-allowed absorption bands for some octahedral chromium(III) complexes [assignment: ${}^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$] and cobalt(III) complexes [assignment: ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$]. For chromium(III) this wavenumber is a direct measure of Δ, eqn. (1), while for cobalt(III) a correction has to be made. Knowing the position also of the maximum of the second spin-allowed absorption band, ${}^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$, and the ratio between the Racah parameters C and B, this correction can be calculated using the d^6 energy matrices of the expanded radial function model, given by Tanabe and Sugano.[34] The ratio mentioned is not known but is likely to lie in the region between 4 and 5.5. The table clearly shows that even though the numerical value of Δ does depend on the choice of the ratio C/B neither the spectrochemical series nor the trend of energy ratios between corresponding cobalt and chromium quantities (the last three rows of the table) are influenced by this choice. It is remarkable that the semi-theoretical ratios of the last two rows are no better than the purely empirical ratio between the wavenumbers, given in the third from last row. The value 21.10 kK for $\sigma_1([Co(NH_3)_6]^{+3})$ used in connection with eqn. (8) was measured here using the same instrument as that used for the other cobalt complexes.

$X^{x-}=$	H_2O	$C_2O_4^{2-}$	NH_3	en	CN^-
$\sigma_1([CrX_6]^{3-x})$	17.40	17.48	21.50	21.90	26.60
$\sigma_1([CoX_6]^{3-x})$	16.50	16.60	21.20	21.55	32.00
$\Delta([CoX_6]^{3-x});\ C=4B$	18.16	18.02	22.87	23.17	33.45
$\Delta([CoX_6]^{3-x});\ C=5.5B$	18.76	18.54	23.48	23.75	33.98
$\sigma_1([CoX_6]^{3-x})/\sigma_1([CrX_6]^{3-x})$	0.95	0.95	0.97	0.98	1.20
$\Delta([CoX_6]^{3-x})/\Delta([CrX_6]^{3-x});\ C=4B$	1.04	1.03	1.06	1.06	1.26
$\Delta([CoX_6]^{3-x})/\Delta([CrX_6]^{3-x});\ C=5.5B$	1.08	1.06	1.09	1.08	1.28

The value 1.05 (Table 1) of eqn. (4) is a lower limit for the ratio $\Delta_{\sigma\text{CN}^-}(\text{Co})/\Delta_{\sigma\text{CN}^-}(\text{Cr})$, since the extra π-stabilization in $[\text{Co(CN)}_6]^{3-}$ as a secondary effect would increase $\Delta_{\sigma\text{CN}^-}(\text{Co})$ relative to $\Delta_{\sigma\text{CN}^-}(\text{Cr})$. If, however, one assumes $\Delta_{\sigma\text{CN}^-}(\text{Co})/\Delta_{\sigma\text{CN}^-}(\text{Cr}) = 1.05$ the quantity $\delta_{\pi\text{CN}^-} = \Delta_{\pi\text{CN}^-}(\text{Co}) - \Delta_{\pi\text{CN}^-}(\text{Cr})$ can be estimated. If $\Delta_{\pi\text{CN}^-}(\text{Cr})$ is known $\delta_{\pi\text{CN}^-}$ can within the assumptions be calculated exactly, but it turns out that $\delta_{\pi\text{CN}^-}$ varies very little with $\Delta_{\pi\text{CN}^-}(\text{Cr})$. For example, for $\Delta_{\pi\text{CN}^-}(\text{Cr}) = 0$ and $\Delta_{\pi\text{CN}^-}(\text{Cr}) = -4$ values for $\delta_{\pi\text{CN}^-}$ of -5.5 and -5.7 kK are found, respectively. It further turns out that these $\delta_{\pi\text{CN}^-}$ values are lower limits (*i.e.* upper limits for the absolute values) when 1.05 is a lower limit to $\Delta_{\sigma\text{CN}^-}(\text{Co})/\Delta_{\sigma\text{CN}^-}(\text{Cr})$. In conclusion the difference 6.9 kK between the Δ values referring to $[\text{Co(CN)}_6]^{3-}$ and $[\text{Cr(CN)}_6]^{3-}$ can then be interpreted as due to differences in Δ_σ and Δ_π values of $\delta_{\sigma\text{CN}^-} = 1.3$ kK and $\delta_{\pi\text{CN}^-} = -5.6$ kK, where both numbers represent lower limits.

III. THE AVERAGE ENVIRONMENT RULE AND GAUSSIAN SHAPE OF ABSORPTION BANDS

In the introduction it was mentioned that the spectrochemical series originally was established[1] for $[\text{Co(NH}_3)_5\text{X}]^{(3-x)+}$-type complexes and later rationalized[8] using the expanded radial function model by reference to cubic complexes of $[\text{CoX}_6]^{(3-6x)+}$-type.

Although historically it did not happen so straight-forwardly one may say to-day that this interrelation of spectra for quite different molecules which could never have been theoretically predicted to be possible, was based upon the approximate validity of the empirical rule[24] called the Average Environment Rule.

This rule may be formulated as follows: a given broad absorption band for a mixed-ligand complex $[\text{MX}_a\text{Y}_b]^{(n-ax-by)+}$ (with $a+b=6$), based upon the octahedron, n being the oxidation state of the central ion M, has a maximum position whose wave-number σ is given by

$$\sigma([\text{MX}_a\text{Y}_b]^{(n-ax-by)+}) = \\ (a/6)\sigma([\text{MX}_6]^{(n-6x)+}) + (b/6)\sigma([\text{MY}_6]^{(n-6y)+}) \qquad (5)$$

or, in other words, is a weighted average of the maxima for the cubic complexes $[\text{MX}_6]^{(n-6x)+}$ and $[\text{MY}_6]^{(n-6y)+}$.

The absorption bands, for which the empirical average environment rule was established, always arise from transitions from orbitally non-degenerate ground levels to excited levels which in octahedral symmetry are orbitally triply degenerate. For the lower symmetry complex there is no longer the symmetry requirement that the three components be degenerate and the average environment rule therefore somehow implies that the observed curve can be considered a sum of the components. This is the basic idea behind curve analysis procedures. Particularly for chromium(III) and cobalt(III) complexes the band shape can often be represented approximately by Gaussian error curves using the wavelength λ as the independent[25] variable. This gives the functional expression

$$\varepsilon = \varepsilon_0 \times \exp - [(\lambda - \lambda_0)/(\delta/2(\ln 2)^{\frac{1}{2}})]^2 \qquad (6)$$

where the maximum is at $(\lambda_0, \varepsilon_0)$ and δ is the full half width of the band.

It is useful for the qualitative interpretation of absorption spectra to note a few of the properties[26,27] of a sum of two Gaussians. Firstly, Gaussians with the same positions and half widths add up to a Gaussian with the same values of these parameters and with a height which is the sum of the heights of the components. Secondly, two Gaussians with the same height and the same half width δ can be removed[26] as far as $\delta/(2 \ln 2)^{1/2} = 0.85\ \delta$ away from each other before their sum curve exhibits a minimum. Thirdly, this separation requirement increases when the heights of the component Gaussians are different. When, for example, the height ratio is 2:1 for two Gaussians of the same widths a minimum does not occur between them until their separation is about 1.15 δ, at a separation of 0.85 δ a shoulder just becomes visible and at a separation of 0.5 δ the sum curve looks to the eye completely symmetrical. Fourthly, when a narrow Gaussian is added to a broad one the narrow one makes itself the more conspicuous of them, even when it has a low intensity. This latter point is illustrated in Fig. 1 which shows analyses of the red tail of the absorption spectra of $[\text{Cr(NH}_3)_4(\text{N-N})]^{3+}$ complexes. The foot from the ultraviolet has been represented by an exponential function which for practical purposes is very similar to the lower part of

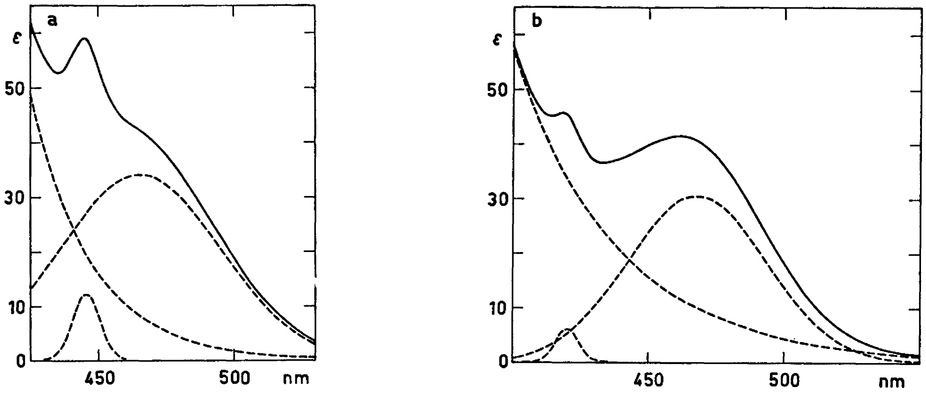

Fig. 1. The red feet of the absorption spectra of $[Cr(NH_3)_4bipy]^{3+}$ (a) and $[Cr(NH_3)_4phen]^{3+}$ (b), (full lines). Each experimental curve was represented by a set of points (λ,ε) which was analyzed by non-linear regression modelling it as a sum (broken lines) of two Gaussians of the form

$\varepsilon_0 \times \exp - [(\lambda - \lambda_0)/(\delta/2(\ln 2)^{\frac{1}{2}})]^2$ and one exponential of the form $h \times \exp - [(\lambda - \lambda_t)/(\delta/2(\ln 2)^{\frac{1}{2}})]$

the latter function in order to account for the absorption toward the ultraviolet. λ_t is the lowest λ value of the (λ,ε) set chosen. The value λ_0 belonging to the broader Gaussian associated with each set refers to the ${}^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$ transition and has in nanometers the values 465.5 ± 2.2 and 467.8 ± 0.2 for the two complexes, respectively, but the standard deviations should be taken *cum grano salis* because the experimental curve is rather badly represented by the model.

a Gaussian. It is noteworthy that even though the ratio between the areas of the large and the small Gaussians is 16 and 30 for the bipy and phen complexes, respectively, the small bands are quite conspicuous. This is because in each case the small band is quite narrow, its width being about 1/6 of that of its broad neighbour.

The qualitative assumption involved here is that an absorption curve can be considered a sum of its electronic components, each one independently provided with width, and the further assumption that these individual components have an approximately Gaussian shape. All the qualitative conclusions which can be drawn on the basis of these assumptions are, apparently without exception, borne out by experiments.

We note the approximate expression for the position of the maximum of the sum curve of ν Gaussians of equal half width and at small separations

$$\nu_0 = \sum_i \nu_i \varepsilon_i / \sum \varepsilon_i \qquad (7)$$

ν_0 is here the wave number position of the maximum of the sum curve whose components' maxima are given by the coordinates (ν_i, ε_i). This expression will be referred to in the following.

IV. RESULTS

1. Cobalt(III) complexes. The position of bipy and phen in the spectrochemical series above ethylenediamine has been considered clear[10,11] for some time for cobalt(III) complexes. Particularly in the case of bipy $[Co\ bipy_3]^{3+}$ exhibits a rather well-isolated (Fig. 2) band $(\lambda_{max}, \varepsilon_{max}) = (449,\ 69.5)$, assigned as ${}^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$, to be compared with the figures (465, 84) for $[Co\ en_3]^{3+}$. However, the $[Co\ phen_3]^{3+}$ complex in this region only exhibits a shoulder on a steep rise in absorption toward the ultraviolet (Fig. 2). For both complexes it is true that intense absorption lies quite near these presumed ligand field bands but recalling the situation with $[Co(NO_2)_6]^{3-}$, one has to be careful. This ion has $(\lambda_{max}, \varepsilon_{max}) = (484,\ 219)$ in this region,[28] *i.e.* its maximum is considerably red-shifted relative to that of $[Co\ en_3]^{3+}$, even though mixed

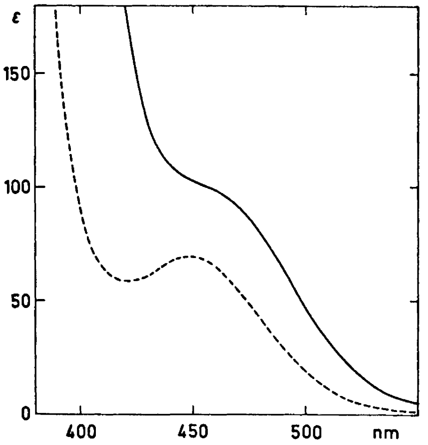

Fig. 2. Visible absorption spectra of $[Co(N\text{-}N)_3]^{3+}$ complexes. Part of the spectra (λ,ε) were analyzed as described in the legend to Fig. 1, here modelling the (λ,ε) set as a sum of one Gaussian and one exponential, the latter referring to the ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ transition.
--- N-N = bipy. Analyzing the spectrum in the interval $400 \leq \lambda \leq 530$ nm gave $(\lambda_0,\varepsilon_0) = (450.9 \pm 0.3, 67.0 \pm 0.2)$. — N-N = phen. Here the analysis was done in two λ-intervals, $425 \leq \lambda \leq 550$ nm and $425 \leq \lambda \leq 535$ nm giving the results for the Gaussians $(\lambda_0,\varepsilon_0) = (457.9 \pm 1.3, 92.4 \pm 1.8)$ and $(459.6 \pm 0.9, 90.5 \pm 1.4)$, respectively. The mean of these two λ_0-values, 459.0 ± 0.7 nm, was used to compare with the results calculated on the basis of the mixed complexes (eqn. 8).

complexes containing NO_2^- together with ethylenediamine and ammonia, by the average environment rule, clearly place the nitro ligand above ethylenediamine in the spectrochemical series. This unusual red-shift found [28] in $[Co(NO_2)_6]^{3-}$ could of course be caused by the chemistry, *i.e.* $[Co(NO_2)_6]^{3-}$ not being present in the solution measured, or some of the NO_2^- ligands being coordinated through oxygen. However, we are not aware of any additional evidence for this and we find it a much more likely explanation that the d^6 level ${}^1T_{1g}$ has been mixed with electron transfer levels or excited levels of the ligands, both of which mechanisms would have to shift the lower energy mixed level toward lower energy. A mechanism of a similar kind might well be at work also in $[Co\ bipy_3]^{3+}$ and $[Co\ phen_3]^{3+}$ in which case the wavenumber position of the pure ligand field transition, ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$, might have been underestimated.

In order to clear up such uncertainties as to the spectrochemical parameters for bipy and phen the spectra of mixed complexes of the type $[Co(NH_3)_{6-2a}(N\text{-}N)_a]^{3+}$ have been measured in this region. The results are given in Table 2.

All the spectra resemble that of $[Co\ bipy_3]^{3+}$ of Fig. 2. However, the band in the 455 nm region is in all cases better isolated because the steep rise in absorption moves toward the ultraviolet as the number of ammonia molecules increases within the complex ions. This can clearly be seen from the positions and absorptivities of the minima given in Table 2.

Introducing the known quantity $\sigma_1([Co(NH_3)_6]^{3+}) = 21\ 100\ cm^{-1}$ and using the average environment rule on the mixed complexes, one obtains for each individual (N-N)-ligand two linear equations to determine the quantity $\sigma_1([Co(N\text{-}N_3]^{3+})$. For example, for $[Co(NH_3)_4bipy]^{3+}$ the equation is

Table 2. Spectral data for $[Co(NH_3)_{6-2a}(N\text{-}N)_a]$ complexes. σ_1 is the wavenumber of the maximum of the ${}^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ transition, σ_{min} that of the minimum before the rise in absorption toward the UV. See fig. 2. The ε quantities are the corresponding molar absorptivities.

	σ_1	ε_1	σ_{min}	ε_{min}
$[Co\ bipy_3]^{3+}$	22 270	69.5	23 750	58.5
$[Co(NH_3)_2bipy_2]^{3+}$	21 880	68.0	25 130	20.0
$[Co(NH_3)_4bipy]^{3+}$	21 440	62.5	25 510	9.5
$[Co(NH_3)_2phen_2]^{3+}$	21 670	72.5	24 180	37.5
$[Co(NH_3)_4phen]^{3+}$	21 340	61.5	25 160	12.0

$$\sigma_1([\mathrm{Co(NH_3)_4bipy}]^{3+}) = \tfrac{2}{3}\times 21\,100 + \tfrac{1}{3}\sigma_1([\mathrm{Co\ bipy_3}]^{3+})$$

corresponding to eqn. (5). Weighting the two equations equally the data from the four last rows of Table 2 give the calculated quantities σ

$$\begin{aligned}&\sigma_1([\mathrm{Co\ bipy_3}]^{3+}) = 22\,200 \pm 100 \quad \text{and}\\ &\sigma_1([\mathrm{Co\ phen_3}]^{3+}) = 21\,890 \pm 100\end{aligned} \tag{8}$$

to be compared with the quantities 22 180 ± 20 and 21 790 ± 40 obtained from Gaussian analyses of the spectra of the *tris*-complexes themselves (see text to Fig. 2).

The mixed complexes under consideration all have the symmetry C_2 so that one would predict from symmetry that the band of cubic parentage $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ would split into three components. Obviously these components lie close to one another as compared with their half-widths and this is the reason why no splitting is observed (*cf.* Section III). It is interesting to note that the assumptions that the levels have a pure cubic parentage [29] and that the components can be represented by Gaussians with the same heights and widths lead to results (eqn. 7) identical to those obtained using the empirical average environment rule (eqn. 5). It is for our present complexes, because of the small splittings, immaterial whether we assume Gaussians as a function of wavenumber or as a function of wavelength.

It should be stressed that the fact that the empirical average environment rule apparently works so well does not allow the conclusion that these assumptions about components are meaningful. On the other hand, it does make such concepts as hidden components and additivity of these attractive until it is actually proved that they are misleading.

2. Chromium(III) complexes. For the tris(N-N)chromium(III) complexes a steep absorption toward the ultraviolet presents problems which from an interpretation point of view are similar to those for cobalt(III), though, in a quantitative sense, they are the more serious for chromium and from a physical point of view probably of a quite different origin.

Also here the spectra of the mixed ammonia-(N-N) complexes have been studied and are depicted and described in Figs. 3 and 1.

In the spectrum of the complex $[\mathrm{Cr(NH_3)_4 phen}]^{3+}$ (Fig. 3) there is a narrow peak at 420 nm, which, when looked at from a component additivity point of view (Fig. 1), is far too narrow to be assigned as the first spin-allowed ligand field band $^4A_{2g}\rightarrow{}^4T_{2g}$ that we are looking for. Even though its position does not exclude the alternative assignment $^4A_{2g}\rightarrow{}^2T_{2g}$ we believe that its intensity is too high for this assignment in view of the fact that it lies too far away from the spin-allowed transitions which, as we shall see below, are expected to lie quite close to those of the $[\mathrm{Cr(NH_3)_6}]^{3+}$ complex which has $\lambda_{\max}\{^4A_{2g}\rightarrow{}^4T_{2g}\} = 465$ nm and $\lambda_{\max}(^4A_{2g}\rightarrow a^4T_{1g}) = 351$ nm. Further, the narrow band under discussion appears to have analogs with a successively enhanced intensity in the complexes $[\mathrm{Cr(NH_3)_2phen_2}]^{3+}$ and $[\mathrm{Cr\ phen_3}]^{3+}$. Its analog at 425 nm in $[\mathrm{Cr\ phen_3}]^{3+}$ was previously assigned [12] as the $^4A_{2g}\rightarrow{}^4T_{2g}$ ligand field band, but our present evidence is that this band is completely covered in the $[\mathrm{Cr\ phen_3}]^{3+}$ complex. A quite nicely separated maximum at 462 nm in the spectrum of the $[\mathrm{Cr(NH_3)_4phen}]^{3+}$ complex and a shoulder in that of $[\mathrm{Cr(NH_3)_2phen_2}]^{3+}$ are associated by us with the ligand field assigment $^4A_{2g}\rightarrow{}^4T_{2g}$ which is consistent not only with their widths but also reasonably well with their molar absorptivities.

From our own previous work [30] it is known that bipy and phen lie close to one another in the hyperchromic series mentioned in section I both being pronouncedly below ethylenediamine. As an example of this one may mention that the $\varepsilon_{\max}$ values for the *cis*-complexes $[\mathrm{Cr\ en_2F_2}]^{+}$, $[\mathrm{Cr\ bipy_2F_2}]^{+}$, $[\mathrm{Cr\ phen_2F_2}]^{+}$ and $[\mathrm{Cr(NH_3)_4F_2}]^{+}$ are 75, 49, 47, and 42, respectively. Recalling that $\varepsilon_{\max}$ for $[\mathrm{Cr(NH_3)_6}]^{3+}$ is 40 one immediately sees that the assignment of the first maximum of $[\mathrm{Cr(NH_3)_4phen}]^{3+}$ is quite reasonable from a molar absorptivity point of view although the Gaussian analyses would place them below ammonia hyperchromically.

This intensity point of view gives us also the clue to the chromium(III) bipyridine systems. Here the steep rise in absorption toward the ultraviolet is even more serious and even in the $[\mathrm{Cr(NH_3)_4bipy}]^{3+}$ complex no ligand field band appears with a separate maximum (Fig. 3). On the other hand with the results from the

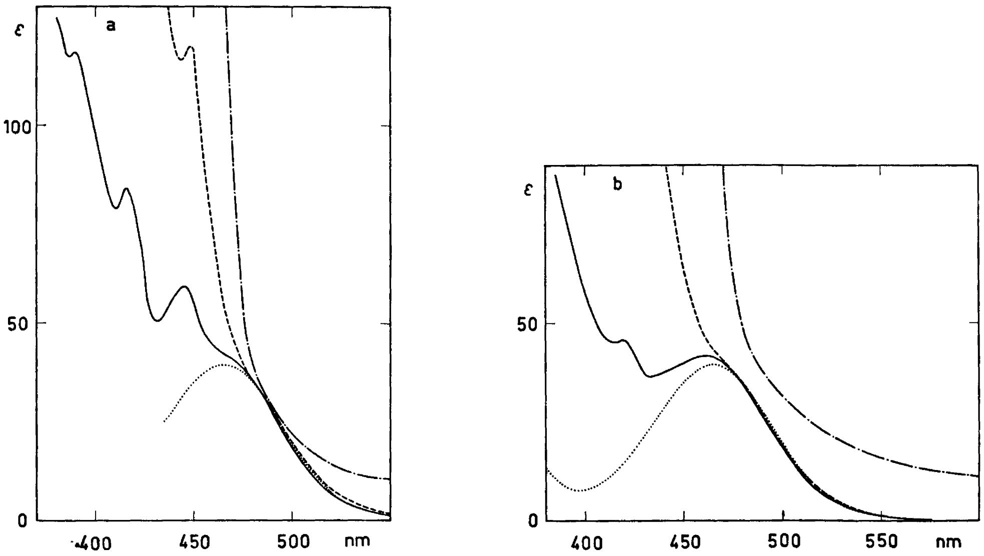

Fig. 3. Visible absorption spectra of $[Cr(NH_3)_{6-2a}(N-N)_a]^{3+}$ complexes. ...., $a=0$; —, $a=1$; ---, $a=2$; —·—·, $a=3$.

(a) $(N-N)=$bipy. The pattern consisting of three maxima shown for $a=1$ at 445, 415, and 390 nm is also found as maxima for $a=2$ and in this case at 450, 420, and 395 nm. For $a=3$ the apparently analogous transitions appear as two shoulders at about 455 and 425 and one maximum at 400 nm.

(b) $(N-N)=$phen. A maximum analogous to that shown for $a=1$ at 420 nm is found as shoulders around 423 and 425 nm for $a=2$ and $a=3$, respectively.

Thus a red-shift of both these patterns, characteristic for chromium(III) complexes with bipy and phen, respectively, is observed when the number of the ligands $(N-N)$ increases.

phen system in mind it is quite clear that the shoulder at about 460 nm fulfils the requirements for the $^4A_{2g}\rightarrow{}^4T_{2g}$ ligand field transition both with respect to width and molar absorptivity (Fig. 1). It may further be noted that the weakly indicated shoulder at almost the same wave-length in the spectrum of the $[Cr(NH_3)_2bipy_2]^{3+}$ complex supports the assignment.

Previous authors when assigning the $^4A_{2g}\rightarrow{}^4T_{2g}$ ligand field transition in $[Cr\ bipy_3]^{3+}$ have chosen either the longest wave-length shoulder [12] at 455 nm or an average [13] of the three narrow bands, 425 nm. We believe that these assignments are out of the question alone because of their small widths (see here Fig. 1). Further evidence is that the three narrow bands occur in all three bipy complexes and apparently have an intensity that increases with the number of bipy molecules in the complex (see text to Fig. 3).

The Gaussian analyses (Fig. 1) make it possible to estimate the positions of the maxima corresponding to the $^4A_{2g}\rightarrow{}^4T_{2g}(O_h)$ transitions in the $[Cr(NH_3)_4(N\text{-}N)]^{3+}$ complexes for both (N-N)-ligands and when these estimates are combined with $\sigma_1([Cr(NH_3)_6{}^3]^{3+})=21\ 500$ cm^{-1}, according to eqn. (5) the following results are obtained

$$\begin{aligned}&\sigma_1([Cr\ bipy_3]^{3+}=21\ 440\pm300\ \text{cm}^{-1}\\&\sigma_1([Cr\ phen_3]^{3+}=21\ 140\pm30\ \text{cm}^{-1}\end{aligned}\qquad(9)$$

where the standard deviations given, as required by eqn. (5), are three times those found by the Gaussian analyses of Fig. 1. As stated previously they should, however, be taken with a certain reservation.

V. DISCUSSION

Until the present time bipyridine and phenanthroline have only been placed in the spectro-

Table 3. Experimental [8] and calculated values for the wave-numbers σ_1, σ_2, and σ_3, of the three spin-allowed transitions of nickel complexes treated using the expanded radial function model [6] for cubic complexes. For $[Ni(NH_3)]_6^{2+}$ and $[Ni\ en_3]^{2+}$ a least squares treatment with equal weighting has been used and the two resulting independent empirical parameters Δ [eqn. (1)] and B [the Racah parameter] are given together with the field strength parameter [31] $\sum = \Delta/B$. For the complexes with the heteroaromatic ligands σ_3 is not observable and the calculation has no degrees of freedom, and therefore only represents a non-linear transformation of the experimental wave-numbers into the set of empirical parameters using the energy matrices of the model. The calculated σ values have in these cases been given in parentheses. Numbers in kK (except last column).

	σ_1	σ_2	σ_3	Δ	B	$\sum$	
$[Ni(NH_3)_6]^{2+}$	10.80	17.50	28.20				exp
	10.89	17.40	28.20	10.89	0.864	12.60	calc.
$[Ni\ en_3]^{2+}$	11.60	18.35	29.00				exp
	11.65	18.28	29.03	11.65	0.825	14.13	calc.
$[Ni\ bipy_3]^{2+}$	12.10	19.20					exp
	(12.10)	(19.20)		12.10	0.917	13.19	calc.
	(12.20)	(19.20)		12.20	0.879	13.88	calc.
$[Ni\ phen_3]^{2+}$	12.20	19.30					exp
	(12.20)	(19.30)		12.20	0.908	13.44	calc.

chemical series with the central ion nickel(II). Jørgensen [8] measured the nickel(II) tris complexes with these ligands and obtained values for the wavenumbers σ_1 and σ_2 of the two lowest energy spin-allowed transitions which assigned cubically are ${}^3A_{2g}\rightarrow{}^3T_{2g}(O_h)$ and ${}^3A_{2g}\rightarrow a{}^3T_{1g}(O_h)$. The third band of wavenumber σ_3, corresponding to ${}^3A_{2g}\rightarrow b{}^3T_{1g}(O_h)$, was not observable because of absorption of other origin than $d-d$ transitions in this region. Jørgensen's values for σ_1 are estimates which are made uncertain by the observed mixing of the ${}^1E_g$ and ${}^3T_{2g}$ excited states. Even the order of the two ligands (bipy < phen)is not quite certain, being based mainly upon the fact that such an inequality applies to the σ_2 values. In Table 3 we give Jørgensen's experimental results and estimations including also his values for $[Ni(NH_3)_6]^{2+}$ and $[Ni\ en_3]^{2+}$. For these two latter ions we have used the wavenumbers of all three spin-allowed transitions to determine the two independent empirical parameters Δ and B placing ammonia and ethylenediamine in their usual order in the spectrochemical and nephelauxetic series. In addition to the derived empirical parameter, the field strength parameter,[31] $\sum = \Delta/B$, which alone is responsible for the extent to which the cubic subconfigurations are mixed, or for that matter, the extent to which the gaseous multiplet terms ${}^3F$ and ${}^3P$ are mixed, has been given. For the $[Ni(N\text{-}N)_3]^{2+}$ complexes σ_1 and σ_2 have been used to calculate the same parameters. It is a consequence of the expanded radial function model [6] that $(\partial\sigma_2/\partial B)_\Delta = 3.2$ for $\sum = 13$. Therefore the fact that σ_2 is found to be 100 cm^{-1} higher for $[Ni\ phen_3]^{2+}$ than for $[Ni\ bipy_3]^{2+}$ need not imply that Δ is also higher but can alternatively be explained by Δ being the same but B being about 30 cm^{-1} higher. In this connection the experimental fact that the minimum between the first and the second spin-allowed transitions is blue-shifted by more than 100 cm^{-1} on going from $[Ni\ phen_3]^{2+}$ to $[Ni\ bipy_3]^{2+}$, has made us include an estimation of 12.2 kK for σ_1 for $[Ni\ bipy_3]^{2+}$ as an alternative to the value 12.1 kK, given by Jørgensen. These numbers are, of course, in themselves not very important but Table 3 shows clearly that all the empirical parameters are only good to within a few per cent. Therefore the two ligands (N-N) cannot be distinguished parametrically but it is probably safe to place them relative to ammonia and ethylenediamine at three different places in the three semi-empirical series

$$\begin{array}{ll} \Delta & \mathrm{NH_3} < \mathrm{en} < \mathrm{N\text{-}N} \\ B_0 - B & \mathrm{N\text{-}N} < \mathrm{NH_3} < \mathrm{en} \\ \sum & \mathrm{NH_3} < \mathrm{N-N} < \mathrm{en} \end{array} \qquad (10)$$

where B_0 is the Racah parameter of the gaseous nickel(II) ion. It has to our knowledge not been noted before that the N-N ligands are less nephelauxetic than ammonia and ethylenediamine. It is, however, not too surprising in view of their low position in the hyperchromic series.

Turning our attention now to cobalt(III) and comparing the σ_1 values of the expression (8) with $\sigma_1([\mathrm{Co(NH_3)_6}]^{3+}) =$ 21 100 cm^{-1} and $\sigma_1([\mathrm{Co\ en_3}]^{3+}) = 21\,500$ cm^{-1} we see that both bipy and phen give rise to σ_1-values above that of ethylenediamine. Using the same correction $\Delta - \sigma_1$ as that for $[\mathrm{Co\ en_3}]^{3+}$ (Table 1) we obtain

$$\begin{array}{l} \Delta([\mathrm{Co\ bipy_3}]^{3+}) = 23\,800;\ \Delta([\mathrm{Co\ phen_3}]^{3+}) = 23\,500;\ C/B = 4 \text{ or} \\ \Delta([\mathrm{Co\ bipy_3}]^{3+}) = 24\,400;\ \Delta([\mathrm{Co\ phen_3}]^{3+}) = 24\,100;\ C/B = 5.5 \end{array} \qquad (11)$$

to be compared with the values for other complexes of cobalt(III) given in Table 1. The spectrochemical series for cobalt(III) then is

$$\Delta \qquad \mathrm{NH_3} < \mathrm{en} < \mathrm{phen} < \mathrm{bipy}$$

where the relative position of bipy and phen is small but significant and also in agreement with our recent findings [30] based upon *cis*-bis(N-N) complexes.

For chromium(III) the situation is different. While for cobalt(III) the average environment rule was checked simultaneously with providing the estimates of σ_1 values for the tris-(N-N) complexes, this is not so for chromium(III). Here we have had to rely on the validity of this rule which on the other hand is more likely to be true for chromium(III) than for cobalt(III) using the π back-bonding argument (see below). The results obtained for chromium (III) place both heteroaromatic ligands with certainty below ethylenediamine in the Δ series

$$\Delta \qquad \mathrm{phen} < \mathrm{bipy} \gtrsim \mathrm{NH_3} < \mathrm{en}$$

but the position relative to ammonia is less certain in view of the uncertainties associated with the curve analysis procedures (Fig. 1). However, the relative position of the two (N-N) ligands is in agreement with the results suggested [30] by the spectra of *cis*-bis(N-N) chromium(III) complexes.

Comparing σ_1 values for corresponding systems of cobalt(III) and chromium(III) by calculating their ratios (eqns. 8 and 9) one obtains

$$\sigma_1([\mathrm{Co\ bipy_3}]^{3+})/\sigma_1([\mathrm{Cr\ bipy_3}]^{3+}) = 1.04 \pm 0.02$$

$$\sigma_1([\mathrm{Co\ phen_3}]^{3+})/\sigma_1([\mathrm{Cr\ phen_3}]^{3+}) = 1.04 \pm 0.01$$

Even though the standard deviations here do not have their proper significance, it is clear that the ratios obtained place these ligands in the region outside the first four ligands of Table 1 whose corresponding ratios are 0.963 ± 0.015.

Comparing the Δ values (for $C/B = 4$) for cobalt(III) (N-N) complexes (eqn. 11) with those for chromium(III) (eqn. 9) it is seen that for both (N-N) ligands Δ(Co) is 2.4 kK higher than Δ(Cr). Using the same assumptions and arguments as those presented at the end of Section II for the ligand CN$^-$ it is possible to separate this Δ difference into a σ and a π component. The results are

$$\delta_{\sigma(\mathrm{N\text{-}N})} = \Delta_{\sigma(\mathrm{N\text{-}N})}(\mathrm{Co}) - \Delta_{\sigma(\mathrm{N\text{-}N})}(\mathrm{Cr}) = 1.0 \text{ kK}$$

$$\delta_{\pi(\mathrm{N\text{-}N})} = \Delta_{\pi(\mathrm{N\text{-}N})}(\mathrm{Co}) - \Delta_{\pi(\mathrm{N\text{-}N})}(\mathrm{Cr}) = -1.4 \text{ kK}$$

and, as with the CN$^-$ complexes, the values both represent lower limits.

We see through this discussion that there is ligand field theoretical evidence for weak π back-bonding in these complexes, though much weaker than in cyanide complexes. The qualitative arguments for ligand field evidence for π acceptor properties discussed in section II and quantitatively documented in Table 1, are based upon a comparison of d^6 and d^3 systems. In previous work [32] concerned with pyridine complexes of chromium(III) the higher acidity of $[\mathrm{Co\ py_4(H_2O)_2}]^{3+}$ as compared with $[\mathrm{Cr\ py_4\ (H_2O)_2}]^{3+}$ was also taken as evidence for cobalt(III) being the better donor of π-electrons.

From infrared evidence it is well-known that carbon mono-oxide molecules, at least when several of them are bound to the same metal ion, show a certain mutual limitating influence upon each other in the sense that their π back-bonding can be enhanced by replacing, for example, three out of six carbon mono-oxide molecules by one molecule such as diethylenetriamine which is unable to act as a π acceptor. Having had trouble with the interpretation of the spectra of *cis*-bis(N-N) complexes, which we published [30] without comments, we had expected in our work a similar mutual influence upon the σ_1 values, which would have made the average environment rule break down in such a way that the $\sigma_1([Co(N\text{-}N)_3]^{3+})$ values calculated from the mixed complexes should be higher the lower the number of (N-N) molecules in the complexes. However, this does not seem to be the case, at least not when the other ligands are ammonia molecules, and the results of the present paper thus provide no evidence for the breakdown of the additive [18] ligand field.

VI. EXPERIMENTAL

Analyses and absorption spectra. C, H, N and Cl analyses were carried out by the microanalytical laboratory of this institute, using standard procedures. Absorption spectra of aqueous solutions (10^{-3} M in hydrochloric acid) of the compounds were recorded using either a Cary Model 118 spectrophotometer (chromium(III) complexes) or a Beckman Model Acta III spectrophotometer (cobalt(III) complexes).

Preparations

1. Chromium(III) complexes. *cis*-$[Cr(NH_3)_2bipy_2](ClO_4)_3$, $[Cr(NH_3)_4bipy](ClO_4)_3.H_2O$, *cis*-$[Cr(NH_3)_2phen_2](ClO_4)_3.3H_2O$, and $[Cr(NH_3)_4phen](ClO_4)_3\cdot\frac{1}{2}H_2O$.

Crude *cis*-dibromobis(N-N)chromium(III) bromide [30] (3 g), dried at 110 °C for several hours, was treated with liquid ammonia (100 ml) in a steel autoclave at room temperature overnight. Excess ammonia was allowed to evaporate at 1 atm in the air, and the moist brownish product was dissolved in water and neutralized with hydrochloric acid. The components of this yellow solution were separated on a column of Sephadex C 25 using a solution which was 0.3 M in lithium chloride and 0.01 M in hydrochloric acid as the eluent. The first red fraction was discarded and the following yellow fractions of first $[Cr(NH_3)_2(N\text{-}N)_2]^{3+}$ and then $[Cr(NH_3)_4(N\text{-}N)]^{3+}$ (10 – 20 % and 30 – 40 % of initial chromium, respectively) were collected. Each such eluate fraction was treated in the following way: it was diluted 5 times with water and stirred with about 5 times the calculated amount of Sephadex C 25 for one hour, when the yellow Sephadex was filtered off from the colourless solution, washed with water, and placed on the top of a new short column containing about 5 times as much Sephadex as the yellow top layer. Elution with 0.2 M sodium acetate, adjusted to pH ~ 7 with acetic acid forced red hydroxo complexes through the column preceding the slowly moving yellow complex. After the impurities had been removed, the complex was taken out using 5 M lithium chloride and crystallised directly in the eluate as perchlorate by the addition of lithium perchlorate trihydrate (2 – 5 g) followed by cooling at 0 °C. The yellow perchlorate was washed with ethanol and dried in the air. All the compounds were analysed for Cr, C, H, N, and Cl. The absorption spectra are depicted in Fig. 3.

2. Cobalt(III) complexes. $[Cobipy_3](ClO_4)_3.3H_2O$, *cis*-$[Co(NH_3)_2bipy_2](ClO_4)_3.2H_2O$, $[Co(NH_3)_4bipy](ClO_4)_3.\frac{1}{2}H_2O$, $[Cophen_3](ClO_4)_3.2H_2O$. *cis*-$[Co(NH_3)_2phen_2](ClO_4)_3.H_2O$, and $[Co(NH_3)_4phen](ClO_4)_3$.

cis-Dichlorobis(N-N)cobalt(III) chloride [30] (2 g) was stirred at room temperature for a couple of hours with a solution (20 ml) which contained ammonium chloride (4.5 M) and ammonia (1.5 M) and to which charcoal (0.2 g) had been added. The charcoal was filtered off and the components of the yellow filtrate were separated on a column of Sephadex C 25 using a solution which was 0.4 M in lithium chloride and 0.01 M in hydrochloric acid as the eluent, the procedure being otherwise identical to that described for the chromium complexes. However, with the cobalt complexes the cleaning procedure with sodium acetate was found to be unnecessary. The first minor red band was discarded and three yellow bands of $[Co(NH_3)_{6-2a}(N\text{-}N)_a]^{3+}$ ($a = 3$, 2, and 1) were collected in the same order as with the corresponding chromium complexes, *i.e.* that of decreasing a (about 20, 50 and 20 % for $a = 3$, 2, and 1, respectively, of initial cobalt). For crystallization, the addition of a little water to the concentrated eluate (5 M in lithium chloride) was found to improve the yield. Recrystallization from dilute perchloric acid (50→0 °C) gave in all cases the pure perchlorate salt (anal Co, C, H, N, and Cl). The spectral data are given in Table 2 and Fig. 2.

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