

Outer-sphere Anion–Anion Complexes

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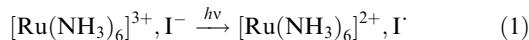
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Bands resulting from contact outer-sphere anion–anion interactions, have been found in the electronic absorption spectra of systems containing simultaneously the anions $[\text{FeNO}(\text{CN})_5]^{2-}$ or $[\text{Co edta}]^-$ and nucleophilic anions (I^- , SCN^- and $\text{S}_2\text{O}_3^{2-}$); the fraction of complex anions occurring in the contact interaction with nucleophilic anions can be as high as several tens of percent in concentrated solutions.

When one of the ions forming an ion pair on interaction in solution is a weak oxidising agent and the other is a weak reducing agent, and no redox reaction takes place between them, changes stable over time are observed in the electronic absorption spectra (EAS). These are attributable to charge transfer from a reducing ion to an oxidising ion,^{1–4} e.g. reaction (1).



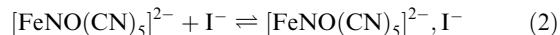
In previous work we were able to detect a spectral manifestation of the outer-sphere interaction between two anions in systems simultaneously containing both the $[\text{FeNO}(\text{CN})_5]^{2-}$ and various nucleophilic ions.^{5,6} Studies by Khoshtariya *et al.*^{7–9} confirm our attributions of observed absorption bands in similar systems. The present work contains the results of further study on this phenomenon in systems containing the low-charged $[\text{FeNO}(\text{CN})_5]^{2-}$ or $[\text{Co edta}]^-$ anion complexes of transition metals and one of the nucleophilic anions I^- , SCN^- or $\text{S}_2\text{O}_3^{2-}$. More detailed results of this study are given in ref. 10.

When $[\text{Co edta}]^-$ (H_4edta = ethylenediaminetetraacetic acid) or $[\text{FeNO}(\text{CN})_5]^{2-}$, which are inert complexes and weak single-electron oxidising agents, weakly absorbing in the near UV range of EAS, and one of the nucleophilic anions I^- , SCN^- or $\text{S}_2\text{O}_3^{2-}$ are present in solution simultaneously, an additional absorption, independent of the inherent absorption of the ions, appears in the EAS. Maxima of the corresponding bands in the different spectra¹ fall within the frequency range $> 31000 \text{ cm}^{-1}$.¹⁰ The positions of the maxima of long-wave absorption bands (ν_{max}) and the band half-widths ($\nu_{1/2}$), deduced by breaking differential spectra down to Gaussian components (for complex anion – iodide ion systems), are given in Table 1. We have not succeeded in observing short-wave absorption bands due to high self-absorption of anions in the frequency range $> 35000 \text{ cm}^{-1}$.

To assign the observed bands we measured the optical density in the $[\text{FeNO}(\text{CN})_5]^{2-}\text{I}^-$ and $[\text{Co edta}]^-\text{I}^-$ systems as functions of the component concentrations. With a constant KI concentration of 3 M the dependence of optical density on the concentrations of the complex ions in the range 5×10^{-4} – 2×10^{-2} M have the shape of a straight line passing through the origin. The dependence of optical density on KI concentration at constant solution ion strength in the initial region of the curves are also close to linear. It is necessary to note that replacement of potassium cations by other alkali metal cations leaves the absorption intensities in the EAS unaffected, within the limits of experimental error.

The intensity of the observed absorption bands depends on the concentrations of both complex and nucleophilic anions, and is independent of the nature of the counter ion. These

facts, together with the absence of changes in the inherent absorption of complex ions in the visible part of the EAS, suggest that the appearance of new absorption bands in the spectra of the systems under study results from the formation of the outer-sphere complex compounds involving two anions, e.g. reaction (2).



Henceforth we will call such associates anion pairs.

The position of new bands in the EAS of the systems under study must be in agreement with the donor–acceptor properties of the ions forming an anion pair. We have made the corresponding analysis on the basis of the simplest approximation of the adiabatic theory of intersphere electron transfer in solution and found¹⁰ that the energies of spectral transitions in anion pairs agree well with the donor–acceptor properties of the ions. These energies depend on the nature of the lowest vacant orbital of the complex ion, which is prone to a quite considerable change when it is populated.

Thus, the data obtained allow us to attribute new absorption bands to the charge transfer from nucleophilic anions to electrophilic anions following their contact intersphere interaction.

To estimate the equilibrium constants for reaction (2) we have investigated the experimental relationship between the optical density in the anion pair absorption band range and iodide concentration using the Benesi–Hildebrand equation. Table 1 shows the calculated extinction coefficients at the maxima of the corresponding absorption bands (ϵ) and the formation constants of the anion pairs (K_{AP}), which allowed us to calculate the fraction of complex ions existing in the form of light-absorbing associates. The latter values for 3 M KI solutions are 0.23 ± 0.04 for $[\text{FeNO}(\text{CN})_5]^{2-}$ and 0.43 ± 0.04 for $[\text{Co edta}]^-$, respectively.

Absorption by anion pairs in the systems under study depends on the solution ionic strength, an increase in which results in an increase in optical density. To explain this relation we invoked the ionic association theory and applied to our systems the Fuoss equation,¹¹ which connects the formation constant of contact ion pairs with the solution ionic strength. The best agreement between the thermodynamic stability constants of anion pairs, calculated by this equation and found for solutions with constant and varied ionic strength, is achieved with an interion distance of 4.6 Å for $[\text{FeNO}(\text{CN})_5]^{2-}\text{I}^-$ and 5.0 Å for $[\text{Co edta}]^-\text{I}^-$, similar to analogous distances for the normal ion pairs.¹² The constants themselves in this case are 0.011 , 0.011 ± 0.002 and 0.010 ± 0.003 for the first pair and 0.076 , 0.086 ± 0.012 and 0.072 ± 0.015 for the second pair. These results suggest that the ionic association theory, and the Fuoss equation in

Table 1 Anion pair characteristics obtained from spectral data (notations in the text).

Anion pair	$\nu_{\text{max}}/\text{cm}^{-1}$	$\nu_{1/2}/\text{cm}^{-1}$	$K_{\text{AP}}/\text{dm}^3 \text{ mol}^{-1}$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$
$[\text{FeNO}(\text{CN})_5]^{2-}, \text{I}^-$	31000 ± 100	7500 ± 100	0.10 ± 0.02	$1.5 \pm 0.4 \times 10^3$
$[\text{Co edta}]^-, \text{I}^-$	33100 ± 100	6700 ± 100	0.25 ± 0.03	$2.0 \pm 0.2 \times 10^3$

particular, are applicable to a description of ion pair formation.

It is necessary to note that a specific feature of the spectral manifestation of the anion pair formation consists of the fact that they are observable only in solutions with high concentrations of nucleophilic anions and, consequently, high ionic strengths. The analysis accomplished showed¹⁰ that under these conditions the Coulomb interaction is no longer a determining factor in the anion pair formation, and the size of the ions becomes mainly responsible for the contact intersphere interaction, which leads to the possibility of anion pair occurrence.

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