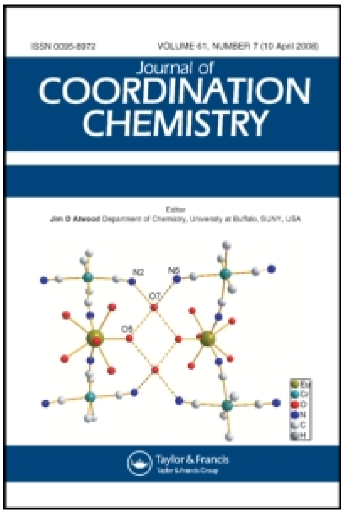

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THE HEXATHIOCYANATOCHROMATE(III) ION IN NON-AQUEOUS SOLUTIONS: A SPECTRAL, ELECTROCHEMICAL AND QUANTUM MECHANICAL STUDY

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Solutions of ammonium hexathiocyanatochromate(III) were made up in acetone (Ac), acetonitrile (An), dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), propanediol-1,2-carbonate (PDC), formamide (FA), *N,N*-dimethylformamide (DMF), tetrahydrofurane (THF) and nitroethane (NE). Cyclic voltammetry was used to investigate electrode reactions on a platinum electrode and half-wave potentials were measured over the temperature range 10–35°C by means of polarography at the dropping-mercury electrode. Both electrochemical and kinetic data are found to exhibit isokinetic relationships which support the interpretation of the solvent effects. Electronic spectra show only small shifts of maxima with change of solvent, but pronounced variations of molar absorbancies. The Cr–N stretching and N–C–S bending frequencies are little influenced by the solvent. Quantum mechanical calculations were carried out with CNDO/2 and MNDO models. The results of the former method are rejected as they yield too small a charge on the chromium centre and a large solvent effect on this charge, not as is reflected in the electronic spectra. The MNDO results reflect the observed spectral changes and, by changes in the effective charges on the coordinated nitrogens, solvents–ligand exchange data.

Keywords: Hexathiocyanatochromates, polarography, solvatochromism, isokinetic relationships, CNDO/2, MNDO calculations

INTRODUCTION

Solvato- and thermochromism of nickel(II) and copper(II) complexes[1–6] is essentially due to differences in the binding of solvent molecules in axial positions (with two chelate ligands already positioned in square planar geometry). Such "inner sphere" interactions often give rise to colour changes that can be used to assign donor numbers to solvents.[2,3] Other complexes such as biscyanobisphenanthroline-iron(II), $[Fe(phen)_2(CN)_2]$, also change their visible spectra in different solvents but without change of ligand in the inner coordination sphere; in fact, biscyanobisphenanthrolineiron(II) can be used as a colour indicator for the ordering of acceptor properties.[4–8]

Reports[7,8] that $(NH_4)_3[Cr(NCS)_6]$ also exhibited visible solvatochromism encouraged us to examine this species in more detail on the basis that its relatively simple structure (regular octahedral coordination) should enable more detailed information to be gained on the role played by the solvent. We were further encouraged in this

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direction by nmr data obtained by Frankel,[9] interpreted as showing that the solvent molecules are essentially orientated along the ligand dipole moment vector of the highly charged $[Cr(CNS)_6]^{3-}$ ion. We report here the results of an investigation of the effect of the solvent on both electrochemical and optical properties of $[Cr(CNS)_6]^{3-}$ and discuss the value of quantum mechanical calculations in describing these results.

EXPERIMENTAL AND THEORETICAL METHODS

$(NH_4)_3[Cr(NCS)_6]$ was prepared by standard methods.[7,10] The solvents and ligands were purified as described elsewhere.[11-13] The water content of the solvents was measured by Karl-Fischer titration and usually found to be less than 30 mg dm^{-3}. Electronic spectra were recorded using a Cary 17D spectrometer and far IR spectra with a Nicolet 20F FTIR spectrometer. The electrochemical investigations were carried out using a non-isothermal cell arrangement with a silver wire reference electrode kept at constant temperature.[14,15] Solutions containing 0.1 mM of the respective complex and 0.1 M $[n\text{-}Bu_4N][B\Phi_4]$ were placed in a thermostatted double-sided cell and pure nitrogen, pre-saturated with solvent, passed through the solution during the experiment. Cyclic voltammetry was performed on platinum as well as on carbon glass electrodes, yielding essentially the same results. Polarographic redox potentials were recorded with respect to bis(biphenyl)chromium(I) tetraphenyloborate (BBCr),[16] either directly, or *versus* ferrocene as intermediate reference substance.

Quantum chemical calculations were performd within the usual CNDO–MO–SCF framework extended to include transition metals.[17] The input parameters have been already described.[18] Molecular geometries for the hexathiocyanatochromate(III) ion were taken from X-ray diffraction data[19,20] for the ammonium salt, whereas the geometry of the surrounding molecules was abstracted from standard compilations[21] and is arranged in accord with the results obtained by Frankel.[9] The MNDO results were derived from single determinant MNDO[22-25] calculations, without inclusion of configuration interactions. The geometrical structures were optimized by the Davidson–Fletcher method.[26,27] Atomic charges correspond to a summation over the squares of the coefficients of the atomic orbitals of all occupied molecular orbitals.[28,29]

RESULTS AND DISCUSSION

Electrochemical investigations

The cyclic voltammograms (on platinum) are essentially the same in their characteristics for all of the investigated solvents. Figure 1 shows as a representative example the cyclic voltammogram of $(NH_4)_3[Cr(NCS)_6]$ in acetonitrile.

The peaks 2 and 5 are related to the Cr(III)/Cr(II) redox couple.[30-32] Peak separations of the cyclic voltammograms are found between 0.2 V (for NE) and 0.7 V (DMSO) showing irreversible behaviour on the Pt electrode. On adding NCS^-, the peak separations decrease, yielding almost reversible behaviour when using 0.1 M $n\text{-}Bu_4NNCS$ as supporting electrolyte. This behaviour can be interpreted in terms of

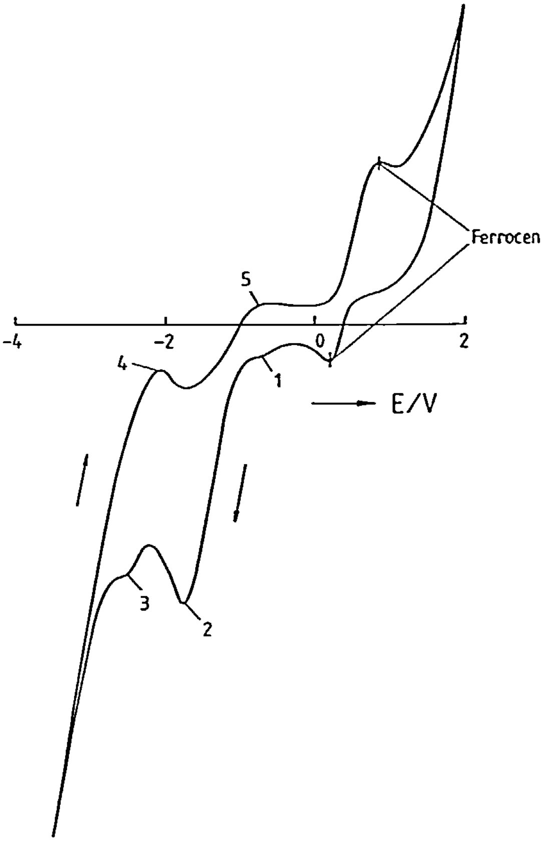

FIGURE 1 Cyclic voltammograms for 10 mM $(NH_4)_3[Cr(NCS)_6]$ and Ferrocene in An (0.1 M n-$Bu_4NB\Phi_4$) on a Pt-electrode (scan rate = 100 mV/s).

reaction (*1*) in which n most probably[30] equals 2. This is superseded by reaction (*2*) when

$$[Cr(NCS)_6]^{3-} + n\mathrm{Solv} \overset{e^-}{\rightleftarrows} [Cr(NCS)_{6-n}(\mathrm{Solv})_n]^{(4-n)-} + n\mathrm{SCN} \qquad (1)$$

$$[Cr(NCS)_6]^{3-} + e^- \rightleftarrows [Cr(NCS)_6]^{4-} \qquad (2)$$

the concentration of NCS^- is sufficiently large. The chemical re-oxidation of Cr(II) is considered to be too slow to be visible under cyclic voltammetric conditions, but it has been suggested that oxidation of the Cr(II) ion due to intramolecular electron transfer with the coordinated solvent molecules can occur, yielding Cr(III) species. An analogous reaction with traces of water or impurities that has been proposed[30] is a disproportionation (*3*).

$$3\,Cr^{II} \rightleftarrows 2\,Cr^{III} + Cr^{0} \qquad (3)$$

Plots of the peak current *versus* the square root of the sweep rate yielded straight lines with slopes related to a one-electron transition. On the dropping mercury electrode, analogous behaviour is observed. Both the application of Kalousek's method and the slopes of logarithmic analyses showed irreversible behaviour (slopes of 95–120 mV), becoming reversible (or nearly reversible in the case of An and DMSO) on the addition of NCS^-, paralleled by a shift of the half wave potentials towards more positive potentials.

The signals labelled 3 and 4 in Figure 1 seem to correspond to irreversible reactions associated with the Cr(II)/Cr(0) redox couple. The signal 4 is shifted towards more negative potentials than signal 3 at lower scan rates. This may be related to the reactions (*4*) and (*5*).

$$[Cr(NCS)_6]^{4-} + 2\,e^- \longrightarrow Cr^0 + 6\,SCN^- \tag{4}$$

$$Cr^0 + 6\,Solv \longrightarrow [Cr(Solv)_6]^{2+} + 2e^- \tag{5}$$

A further irreversible step appears on the addition of NCS^- and is also found in chromium-free NH_4SCN solutions. This can be assigned[33–35] to reaction (*6*).

$$2\,SCN^- \longrightarrow (SCN)_2 + 2\,e^- \tag{6}$$

Polarography at the dropping-mercury electrode enabled only the first reduction step to be resolved in all investigated solvents and this has been measured at various temperatures (see Table I).

TABLE I

Temperature-dependent half-wave potentials for the first reduction step of $(NH_4)_3[Cr(NCS)_6]$ in different solvents (measured against bis(biphenyl)chromium(I) iodide as reference using 0.1 molar *n*-$Bu_4NB\Phi_4$).

Acetone		Acetonitrile		Dimethylsulfoxide	
t/°C	$E_{1/2}$/mV	t/°C	$E_{1/2}$/mV	t/°C	$E_{1/2}$/mV
18.14	−687	20.20	−634	18.25	−799
21.60	−679	23.65	−619	21.75	−798
24.46	−675	27.1	−609	25.2	−797
27.28	−673	31.05	−596		
31.50	−670	34.45	−586		
35.04	−667				

Nitroethane		*N*,*N*-Dimethylformamide	
t/°C	$E_{1/2}$/mV	t/°C	$E_{1/2}$/mV
12.65	−187	19.84	−845
14.7	−182	23.70	−843
19.35	−171	26.33	−840
23.75	−153		
29.05	−146		

Table II shows that increasing temperature leads in all cases to less negative reduction potentials, in other words to less noble properties of the complexes. Half-wave potentials smoothly correlate with the donor number[36] (DN) of the solvent, and not, as would be expected for a negatively charged ion, with the acceptor number (AN)[36-38] (see Fig. 2). This cannot readily be explained by ligand-solvent exchange as proposed in equation (*1*) because it is also found after addition of SCN^- where the inner coordination sphere of the depolarizer should remain fully occupied with NCS^- ions. A more likely explanation, therefore, might concern the presence of low lying acceptor orbitals able to interact with solvent-donor molecules *via* inter-ligand "pocket" positions. Such an interaction has been found in iron(II) and iron(III) phenanthroline complexes.[24,25,28] Note that spectral properties similarly depend upon the donor properties of the solvent (see below), and it might be significant that both CNDO/2 and MNDO calculations yielded suitably small HOMO-LUMO separations of less than 0.15 eV; the latter can of course be interpreted as low lying acceptor orbitals.

TABLE II

Half-wave potentials ($E_{1/2}$) at 25°C using 0.1 molar n-$Bu_4NB\Phi_4$, and their temperature dependence for the first reduction step of $(NH_4)_3[Cr(NCS)_6]$ in different solvents.

solvent	$E_{1/2}$/mV[a]	$\partial E_{1/2}/\partial T$/mV.K^{-1}	m[b]	r[c]
Ac	−675	1.096	6	0.976
An	−615	3.341	5	0.998
DMSO	−797	0.317	3	0.999
NE	−152	2.625	5	0.988
DMF	−842	0.777	3	0.910
THF	−750			

[a] $E_{1/2}$ at 25°C resulting from regression analysis of T-dependent data. [b] Number of data sets obtained at different temperatures. [c] Correlation coefficients for linear regression of $E_{1/2}$ *versus* T.

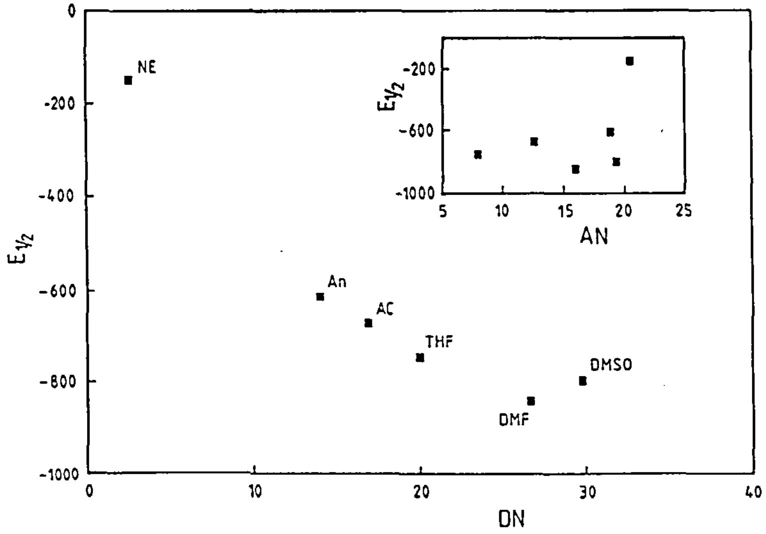

FIGURE 2 Half-wave potentials of $(NH_4)_3[Cr(NCS)_6]$ against BBCr reference *versus* the donor-number of the solvent (insert shows the dependence upon the acceptor number).

The observed temperature coefficients of the half-wave potentials ($\partial E_{1/2}/\partial T$) appear to be largest for An and smallest for DMSO; the half wave potentials in DMSO can be considered to be temperature-independent.

The data have also been analyzed for isoequilibrium behaviour by use of statistical methods.[39-42] Three of the five solvents, namely Ac, DMF and NE, exhibit isoequilibrium behaviour with a negative isokinetic temperature ($T_{iso} \cong -320K$), pointing to the appearance of an anti-compensation effect and in this way supporting a consecutive reaction mechanism. Thus we have an electron transfer step affecting the overall energy change whereas the NCS^- dissociation affects the overall entropy change, with both steps oppositely affected by solvation. Thus, decrease in solvation strength (either donor or acceptor properties) brings about a decrease in the enthalpic term and an increase in the entropic term, respectively. Since the entropic contribution dominates the free energy changes, it follows that the solvation in many cases effectively disfavours reduction. DMSO and An cannot be included in this argument as they are not members of the isoequilibrium group. The results for these simply involve a positive T_{iso}, thus obviating the necessity of invoking a two-step mechanism involving ligand exchange for this pair of solvents.

Lo and Watts[43] also include isokinetic behaviour in their interpretation of kinetic results concerning reaction (*7*),

$$[Cr(NCS)_6]^{3-} + Solv \longrightarrow [Cr(NCS)_5(Solv)]^{2-} + NCS^- \qquad (7)$$

obtaining $T_{iso} = 192K$ for the solvents DMA, DMF and DMSO. Furthermore, the related solvent exchange reaction (*8*) yielded two IKR-series,

$$(NH_4)_2[Cr(NCS)_5(Solv_1)]^{2-} + Solv_2 \longrightarrow (NH_4)_2[Cr(NCS)_5(Solv_2)]^{2-} + Solv_1 \qquad (8)$$

one for DMA, DMF and DMSO taken as $Solv_1$ together with DMF, DMA and DMF as $Solv_2$, and another including DMA, DMF and DMSO as $Solv_1$ with DMSO, DMSO and DMA as $Solv_2$, respectively. For the former series, T_{iso} is 305K and for the latter the value is 320K.

Based on theoretical considerations,[42] the existence of an IKR requires the occurrence of a heat-bath frequency given by equation (*9*) and thus the occurrence of

$$\nu = RT_{iso}/h\,N_L \qquad (9)$$

the IKRs being discussed requires the presence of following vibrational frequencies: for the reaction series (*7*) 133 cm^{-1}, and for the two solvent-exchange series (*8*) 211 cm^{-1} and 222 cm^{-1}, respectively. In agreement with this requirement, IR absorption bands are found for DMA at 150 cm^{-1}, 205 cm^{-1} and 228 cm^{-1}; for DMF at 130 cm^{-1} and 215–250 cm^{-1}; for DMSO[38] at 115 cm^{-1}, 150 cm^{-1}. The IR spectrum of $(NH_4)_3[Cr(NCS)_6]$ itself does not have absorption bands in this region.

Spectral behaviour

The visible spectrum of $(NH_4)_3[Cr(NCS)_6]$ exhibits two absorption bands (the band positions and molar absorbancies (Table III) are slightly smaller than values reported earlier[7]). The bands near 550 nm (λ_1) and 415 nm (λ_2) can be assigned[7,11,46,47] to a transition ${}^4A_{2g} \rightarrow {}^4T_1(F)$ and a ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (directly related

TABLE III

Absorption maxima and corresponding molar absorption coefficients (ε; in $dm^3/mol.cm$) of $(NH_4)_3[Cr(NCS)_6]$ in various solvents at 25°C.

	λ_1/nm	ε_1	λ_2/nm	ε_2	λ_3/nm	ε_3	λ_4/nm	ε_4	λ_5/nm	ε_5	DN	AN
MeOH	552.0	95.0	412	73.5	309.0	27900			235.0	27724	19.1	41.5
An	558.0	107.1	417	95.7	311.0	74390	276	49100	237.5	72424	14.1	18.9
DMSO	552.0	89.1	410	68.7	316.0	51324	277	14100			29.8	19.3
DMF	552.0	90.3	414	73.4	314.0	171700	276.5	60600			26.6	16.0
NE	555.0	109.7	419	100.7							5.0[a]	15.8
EtOH	554.0	99.0	414	82.3	309.5	27840	275.5	32330	235.0	26231	20	37.1
PC	557.5	103.8	416	87.19	313.5	47080			238.0	37632	15.1	18.3
FA	563.5	128.35	420	104.6	315.5	156800					24	39.8
THF	563.5	121.28	420	104.3	317.0	38970			235.5	68750	20	8
Ac	550.0	104.1	415	89.0							17	12.5

[a] DN_B-value from ref. 38.

to 10 Dq) transition for the band, respectively. Both of these transitions should be strongly affected by changes in the ligand field (*c.f.* Tanabe-Sugano diagrams) showing that the present outer-sphere solvent effects hardly affect the ligand field at the coordination centre. A somewhat larger solvent effect on λ_2 than on λ_1 is observed, although greater influence of the ligand field parameter 10 Dq on the position of the first band would be expected from ligand field theory. The small changes in the absorption maxima are accompanied, however, by large changes in the molar absorbances and it is these that are responsible for the solvatochromic behaviour of the $[Cr(NCS)_6]^{3+}$ ion. Since these transitions are Laporte-forbidden, gaining their intensity to a large extent *via* admixture of charge-transfer states, changes in the charge transfer spectra are to be expected. The latter bands are found at 310 nm, 270 nm and 230 nm.

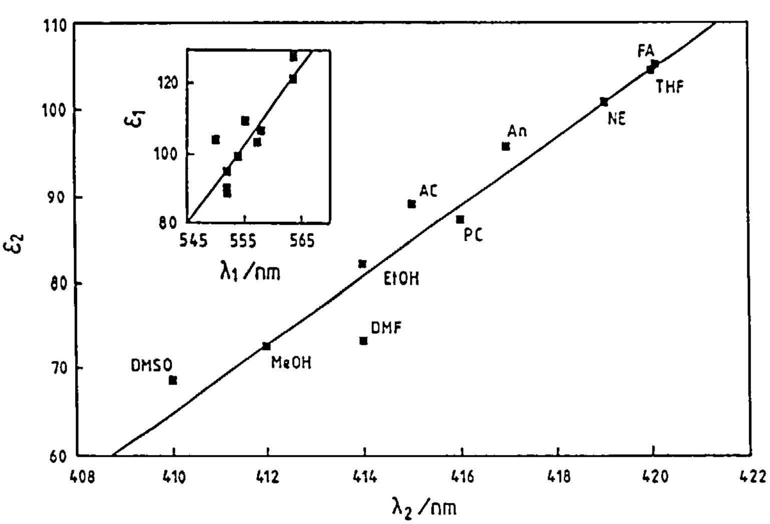

FIGURE 3 Molar extinction coefficients *versus* position of the respective absorption maxima of the d–d transition bands of $(NH_4)_3[Cr(NCS)_6]$ in different solvents.

Increasing molar absorbancies, ε_1 and ε_2, are observed with a red shift (*i.e.*, with decreasing 10 Dq) of the respective absorption maxima in different solvents (Fig. 3). With the exception of FA and THF, all values are linearly related to the donor number[34] of the solvent (see Fig. 4), whereas no such correlation with the acceptor number occurs. This implies that increasing donor properties of the solvent yield increasing 10 Dq values. Although this is to be expected for inner-sphere Cr(III) complexes,[46] it is a surprising result for outer-sphere coordination of a negatively charged anion.[36,37] It is, however, paralleled by the dependence of $E_{1/2}$ upon DN (see above). The solvent induced changes can be interpreted as arising from a change in the electron distribution due to interaction of the solvent molecules with the NCS^- groups. Frankel[9] has concluded from nmr measurements that the solvent molecules in the second coordination sphere are essentially completely oriented along the ligand dipole-moment vector at the strongly charged $Cr(NCS)_6{}^{3-}$ ion (see charge calculations below). The observed changes in the ligand field parameter Dq are in agreement with a pile-up effect[34] on the coordinating N-atom of the thiocyanate ion. Although the band positions of the charge transfer bands and their molar absorbances exhibit, in part, strong solvent dependences, no simple relationships to solvent parameters or to the spectral parameters of the d–d transitions are found. There are no correlations of any one of the spectral parameters with dielectric constant.

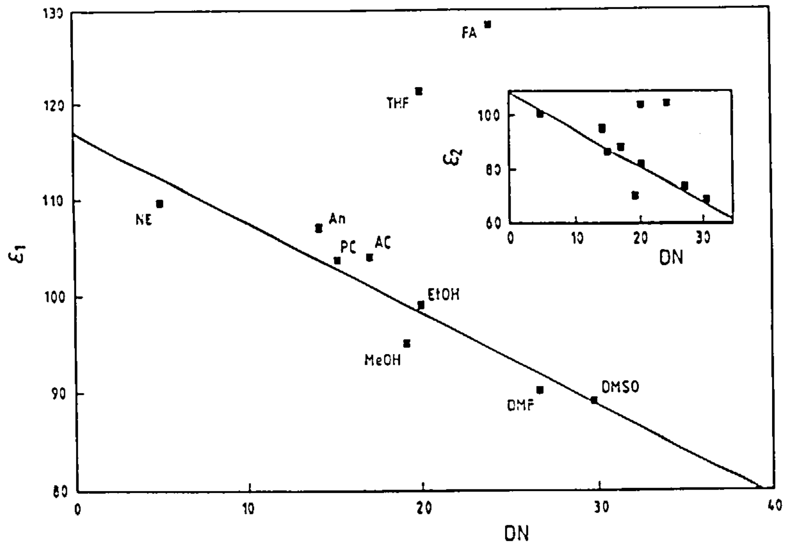

FIGURE 4 Molar extinction coefficients of the d–d transition bands of $(NH_4)_3[Cr(NCS)_6]$ *versus* the donor number DN different solvents.

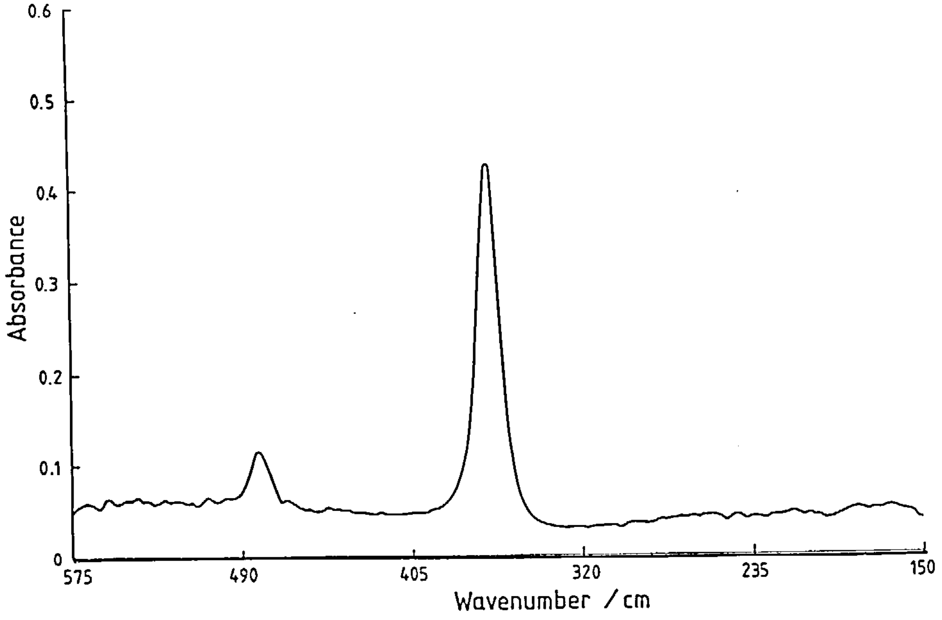

FIGURE 5 Far IR spectrum of $(NH_4)_3[Cr(NCS)_6]$ dissolved in MeOH.

Two absorption bands of $(NH_4)_3[Cr(NCS)_6]$ are found in the far IR region for all investigated solvents. They can be assigned[49-51] to a Cr–N stretching vibration at about 365 cm^{-1} and an N–C–S bending vibration near 480 cm^{-1} (see Fig. 5). IR spectra of the thiocyanato complexes have already shown that the nitrogen atom coordinates to Cr(III) (as would be expected from the rules concerning hard and soft interactions[3,52]). Table IV gives the absorption frequencies and shows only small shifts associated with solvent variation. Although the outer solvent sphere influences the energy and charge distribution of the complex, the result of the interaction is obviously not localized near the coordination centre. In other words, there are no changes in the length of the Cr–N bond, and little at the N–C bond. Both the CNDO/2 and MNDO calculations confirmed this interpretation as almost no changes of bond-orders of the Cr–N and the N–C bonds are found. Only the C–S bond seems to be weakened significantly when interacting with the solvent, in agreement with bond-length variation rules.[34]

TABLE IV

Far IR absorption maxima (cm^{-1}) for $(NH_4)_3[Cr(NCS)_6]$ in different solvents (ν = stretching vibration; δ = bending vibration).

Medium	ν Cr–N	δ N–C–S
Ac	364.5 s	482.0 m
An	366.5 s	484.3 m
DMSO	364.1 s	482.2 m
EtOH	365.5 s	480.1 m
MeOH	365.8 s	481.8 m
n-PrOH	365.3 s	480.9 m
i-PrOH	366.6 s	478.2 m
DMF	—	480.8 m
PDC	364.6 s	482.5 m
CsI	365.0 s	477.6 m

Charge distribution from CNDO/2 and MNDO calculations

The above experimental results may be discussed from the point of view of a semi-empirical quantum mechanical description on the basis of a CNDO/2 and an MNDO model. The calculated charges on the atoms of $[Cr(NCS)_6]^{3-}$ are given in Table V for the free ion and the solvated ion. Solvent molecules are assumed to interact with each of the six coordinated NCS^- ligands in agreement with the interpretation of nmr data by Frankel.[9] Whereas the geometric arrangement of the whole calculated system could be optimized with the MNDO model,[26,27] this was not possible with the CNDO/2 calculations. In turn, this, however, means a restriction on the size of the systems calculated with the MNDO method (because of time and memory requirements).

We begin by noting that the two methods disagree radically as to the charge on the central chromium atom. The CNDO/2 method suggests a very low effective charge whereas the MNDO method suggests little change from that of the free ion. Furthermore, the CNDO/2 results suggest a strong solvent effect on this charge which we would expect to be reflected in the spectra. Table III, however, shows that olvation has little effect on the energy of electronic transitions involving the metal on. Both these results lead us to the belief that the MNDO results give a more ealistic picture of the electronic structure of complexes of this type.

TABLE V
Atomic charges (in atomic units) from a CNDO/2 and an MNDO calculation for $[Cr(NCS)_6]^{3-}$ surrounded by six solvent molecules.

		unsolv.	MeOH	H_2O	An	Ac	DMSO	NE	DMF
		CNDO/2 Results							
Charge on									
	Cr	0.29	0.094	0.12	0.10	0.092	0.11	0.12	0.099
	N	−0.12	−0.13	−0.13	−0.14	−0.14	−0.14	−0.14	−0.136
	C	0.01	0.12	0.12	0.11	0.11	0.11	0.11	0.11
	S	−0.44	−0.44	−0.32	−0.47	−0.47	−0.47	−0.47	−0.47
Solvent[a]		−0.066	−0.19	−0.024	−0.019	−0.026	−0.025	−0.019	
		MNDO Results							
	Cr	2.71	2.7219	2.72	2.72				
	N	−0.360	−0.3580	−0.358	−0.359				
	C	0.0065	0.0294	0.0261	0.0236				
	S	−0.598	−0.6087	−0.607	−0.606				
Solvent[a]		0.0164	0.0141	0.0134					

[a] Sum over all atomic charges of one solvent molecule; *i.e.*, charge transferred to the complex.

When we come to the charges on the ligand atoms, it is interesting to note that the CNDO/2 results suggest that the charges are little affected by interaction with the solvent molecules. Even the directly involved sulfur atoms are relatively little affected. Thus it seems that this calculation treats the NCS group as a non-reacting bridge between solvent and coordination centre. The MNDO results, although limited because of computing difficulties, are more promising; there is a very good linear correlation of charges with donor number; again the greatest effect is seen at the sulfur atom. It is perhaps surprising to see the sulfur atom acting as an acceptor towards the solvent, but this is in agreement with the experimental results discussed above, showing a dependence on the donor rather than the acceptor properties of the solvent. In this respect it is also of interest to note that methanol is an exceptionally strong acceptor within the series of solvents under consideration, and this seems to lead to an anomalous wavelength shift in the visible spectrum (see above). On the other hand, the negative charge at the NCS^- nitrogen atoms decreases with increasing donor number of the attached solvent. The overall effect can therefore be considered as an increasing polarization of the NCS^- ligand with increasing donor properties of the surrounding solvent.

These observations are explicable in terms of a σ attack at the S-atom and a π back-donation through the Cr–N=C=S π-system thus yielding a decrease in electron density at the Cr atom and an increase in electron density at the S atom. The N–C bond is acting as a π-bridge, *i.e.*, both exhibit decreasing electron density with increasing donor properties of the surrounding solvent. The MNDO calculations seem to support this picture as they show changes in electron density at Cr, N, C, and

S in the correct direction. The MNDO calculations (in contradistinction to the CNDO/2 calculations) suggest, however, an overall transfer of charge to the solvent, but this is extremely small and is almost certainly a computational artefact (detailed discussion of the actual charges would not in any case be fruitful, as we believe that two of the solvents calculated with the MNDO method, namely methanol and water, would not behave as simple donors towards the complex ion).

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