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Solvatochromism of Thiocyanato-tetraazamacrocycle-manganese(III) Complexes

J. Burgess*, D. L. Davies, A. J. Grist, J. A. Hall, and **S. A. Parsons**

Chemistry Department, University of Leicester, Leicester, LE1 7RH, United Kingdom

Summary. Solvent effects on the *charge-transfer* bands of a series of thiocyanato-tetraazamacrocycle-manganese(III) complexes are reported, and discussed in terms of the donor and acceptor (hydrogen-bonding) properties of the respective solvents. The piezochromic behaviour of one of these complexes is also described.

Keywords. Donor number; Acceptor number; Manganese complexes; Tetraazamacrocyclic ligands; Charge-transfer spectra; Solvation.

Solvatochromie von Thiocyanato-Tetraazamakrocyclo-Mangan(III) – Komplexen

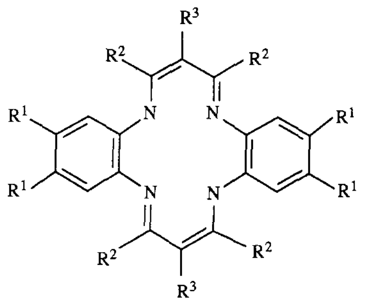
Zusammenfassung. Die Auswirkung von Lösungsmitteleffekten auf die *charge-transfer* – Banden einer Reihe von Thiocyanato-Tetraazamakrocyclo-Mangan(III) – Komplexen wird im Zusammenhang mit den Donor- und Akzeptoreigenschaften des Lösungsmittels diskutiert. Das piezochrome Verhalten eines der Komplexe wird beschrieben.

Introduction

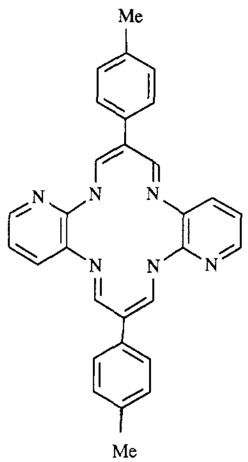
Since the demonstration of large solvent effects on the wavelength of maximum absorption for the metal-to-ligand *charge-transfer* (MLCT) band of dicyanobis(1,10-phenanthroline)-iron(II) nearly forty years ago [1], solvatochromic properties of iron(II)-diimine-cyanide [2], molybdenum(O)-diimine-carbonyl [3], and related complexes [4] have been examined in considerable detail [5]. Despite the report of modest solvatochromism for the chromium (III) and and cobalt(III) complexes $[Cr(NCS)_6]^{3-}$, $[Cr(NH_3)_2(NCS)_4]^-$, and *cis*-$[Co(en)_2(NCS)_2]^+$ in the original paper on solvatochromic behaviour of transition metal complexes [1], there have been relatively few, and often rather limited, studies of the solvatochromic behaviour of thiocyanate complexes. These studies have involved such complexes as hexathiocyanatochromate(III) [6], *trans*-$[Co(cyclam)(NCS)_2]^+$ [5, 7], and biscyclopentadienylbisthiocyanatotitanium(IV) [8].

Similar comments may be made in relation to pressure effects on MLCT bands. Piezochromic behaviour has been described for a number of iron-diimine-cyanide complexes [9] and molybdenum-diimine-carbonyl compounds [10], but there have apparently been no studies of pressure effects on MLCT (or LMCT) bands of thiocyanate complexes.

We were therefore interested to follow up the report of solvatochromic behaviour of the *charge-transfer* bands of two tetraazamacrocycle-thiocyanate-manganese complexes, $Mn(NCS)L^1$ and $Mn(NCS)L^2$. Charge-transfer energies for these complexes in a range of solvents were reported [11] to correlate with solvent Z values [12]. However, the original investigators did not include donor solvents such as alcohols, N,N-dimethyl formamide (*DMF*), or dimethyl sulphoxide (*DMSO*) in their investigation. We felt that such solvents might well affect charge-transfer energies through interaction at the vacant sixth coordination site at the manganese in the title compounds. We wished to examine this possibility, to attempt to correlate solvatochromic properties of these compounds with those of the inorganic complexes named above, and to investigate pressure effects on their *charge-transfer* spectra. The results of our study, the main conclusion from which is that donor solvent – manganese interactions are important, even dominant in many cases, are reported here.



	R^1	R^2	R^3
L^1	H	H	H
L^2	Me	H	H
L^3	H	Me	H
L^4	H	H	Me
L^5	H	H	4-tolyl



L^6

Experimental Part

The complex $Mn(NCS)L^3$ was prepared by the published method [13]; the other complexes were prepared similarly [12, 13]. The preparation and characterisation of the thiocyanatomanganese complexes of L^4, L^5, and L^6 will be reported in full elsewhere [14].

Visible absorption spectra at atmospheric pressure were run on a Shimadzu UV-160 instrument. Spectra over the pressure range up to 1.25 kbar were run in the thermostatted high pressure cell described elsewhere [15], mounted in the cell compartment of a Pye-Unicam SP 8-100 spectrophotometer. Values for wavelengths of maximum absorption could be read to the nearest 0.5 nm on both instruments.

Results and Discussion

Wavelengths of maximum absorption for our four complexes, containing macrocycles L^3 to L^6, are reported in Table 1. This table also includes a number of solvent parameters of relevance to the following discussion. The entries in this table are ordered according to their *Reichardt* $E_T(30)$ values [16], since such values are available for all the solvents used in this investigation. *Reichardt's* scale is based on a strongly solvatochromic betaine; $E_T(30)$ values correlate fairly closely with *Kosower* Z values [12] (mentioned in the Introduction above), based on the solvatochromic salt 1-ethyl-4-carbomethoxypyridinium iodide. Aceptor numbers (AN) [17], derived from ^{31}P chemical shifts of dissolved triethylphosphine oxide, are related to Z and E_T. Whereas Z, E_T, and AN are, in the present context, essentially measures of hydrogen-bonding interactions, the other two solvent parameters included in Table 1 are measures of electron pair donor capabilities. *Gutmann's* donor numbers (DN) [18], are derived from enthalpies of *Lewis* acid-base adduct formation with the acceptor antimony pentachloride (whence problems arise with establishing values for reactive solvents such as methanol and, especially, water). The λ(Cu) values refer to *charge-transfer* wavelengths for the complex $[Cu(acac)(tmen)]^+$, where acacH = acetylacetone (pentane-2,4-dione) and tmen = N,N-tetramethyl-ethane-1,2-diamine, in the respective solvents [19, 20]. It might be felt that solvent interactions with Cu^{2+} are particularly appropriate for comparisons with our manganese complexes, but it should be added that in practice λ(Cu) and DN values correlate fairly well.

Figure 1 shows the relation of $\lambda_{max}(CT)$ for all six complexes Mn(NCS)L with solvent Z values. Correlations for our four complexes seem slightly less satisfactory than for the earlier-studied L^1 and L^2 complexes [11]. This is partly due to the smaller number of points for the complexes of L^4 and L^6, and partly to the marked

Table 1. Wavelengths of maximum absorption $\{\lambda(CT)\}$ for the *charge-transfer* bands of thiocyanato-tetrazamacrocycle-manganese complexes Mn(NCS)L

Solvent	Solvent parameters					$\lambda(CT)$/nm			
	$E_T(30)$	Z	AN	DN	λ(Cu)	L^3	L^4	L^5	L^6
MeOH	55.5		41.3	(30)	591	565		527	
HOAc	51.2	79.2	52.9	20	589	588	569	561	580
MeCN	46.0	71.3	18.9	14.1	578	599		564	579
DMSO	45.0		19.3	29.8	613	564		533	
DMF	43.8	68.4	16.0	26.6	603	568		533	
TMP	43.6			23.0	599	579		556	
Me_2CO	42.2	65.7	12.5	17.0	571	603		571	
$PhNO_2$	42.0		14.8	4.4	533	605		580	
CH_2Cl_2	41.1	64.2	20.4			604	578	571	589
HMPA	40.9		10.6	38.8		579		578	
$CHCl_3$	39.1	63.2	23.1	4.0		603	583	574	592
EtOAc	38.1	59.4		17.1	577	596	578	569	585
PhCl	37.5	58.0				603		579	
THF	37.4		8.0	20.0	579	592		570	
Dioxan	36.0	(75)	10.8	14.8	575			566	
C_6H_6	34.5	54.0						578	
CCl_4	31.9		8.6					578	
c-C_6H_{12}	31.2							586	

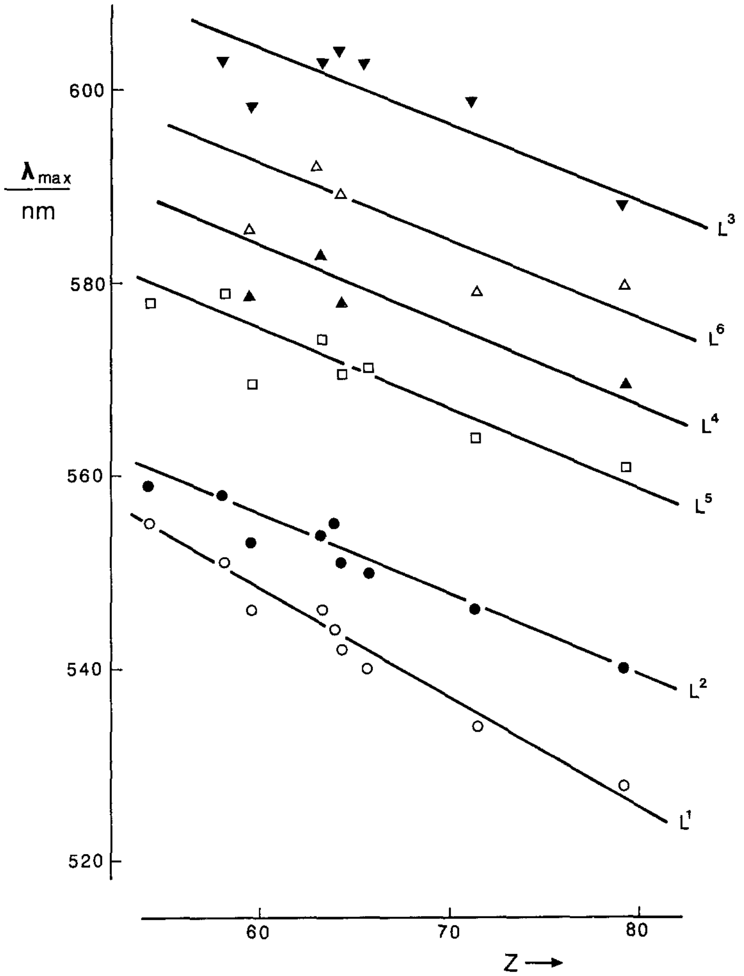


Fig. 1. Comparison of correlations of wavelengths of maximum absorption for the *charge-transfer* bands, $\lambda(CT)$, of complexes Mn(NCS)L, with L = L^1 to L^6, with solvent Z values for solvents used in Ref. [11]

deviation for ethyl acetate as solvent for all six complexes. The trend lines shown on Fig. 1 for the complexes of ligands L^3 to L^6 inclusive have been drawn parallel to that for Mn(NCS)L^2 – they are not the best straight lines (which would have been difficult to estimate for Mn(NCS)L^4 and Mn(NCS)L^6. It is apparent from Fig. 1 that solvent effects on $\lambda_{max}(CT)$ are very similar for all six complexes.

Apart perhaps from ethyl acetate, the results shown in Fig. 1 do not include values from potential donor solvents. In contrast, $\lambda_{max}(CT)$ values for Mn(NCS)L^3 and Mn(NCS)L^5 in a series of solvents with significant donor properties show a marked correlation with solvent donor numbers, DN (Fig. 2). Moreover, λ_{max} for Mn(NCS)L^3 correlates well with λ(Cu), as shown in Fig. 3. Thus, at least for solvents for which DN and λ(Cu) values are available, donor properties have a dominant effect on charge-transfer spectra for complexes Mn(NCS)L.

Although several solvents appear in Fig. 1 and in Figs. 2 and 3, any correlation applicable to all the solvents included in Table 1, *i.e.* to the full range of solvents from water and alcohols through,to hydrocarbon solvents, needs to take account

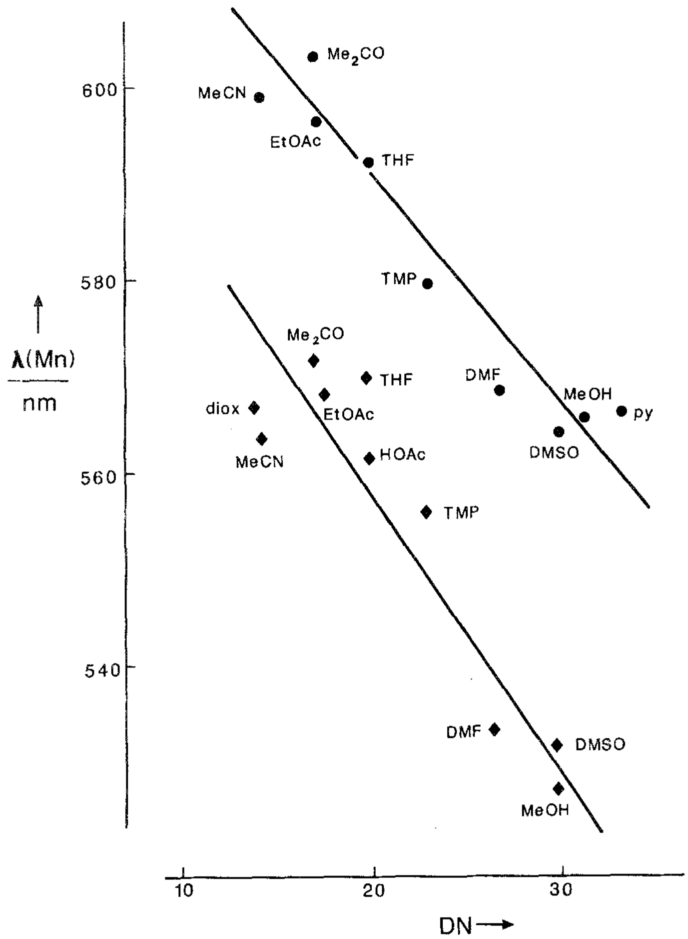


Fig. 2. Correlation of $\lambda(CT)$ for $Mn(NCS)L^3$ (●) and $Mn(NCS)L^5$ (◆) with solvent donor numbers

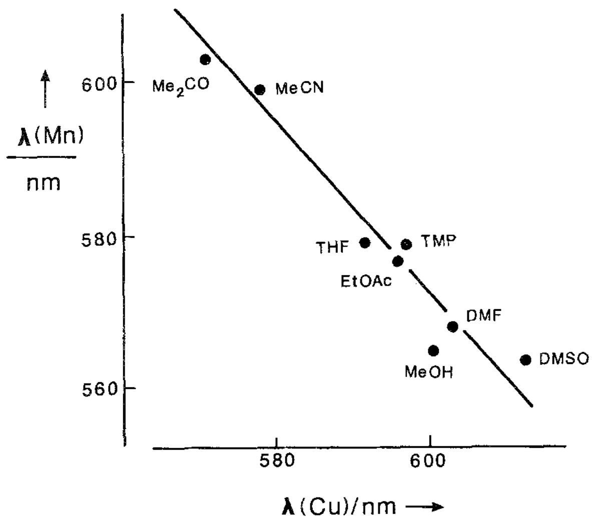


Fig. 3. Correlation of $\lambda(CT)$ for $Mn(NCS)L^3$ with $\lambda(CT)$ for $[Cu(acac)(en)]^+$

of both acceptor and donor properties. This is illustrated, for $Mn(NCS)L^3$ and $Mn(NCS)L^5$, in Figs. 4 and 5. Here $\lambda_{max}(CT)$ values for these two managese complexes are plotted against solvent acceptor numbers. The filled symbols apply to solvents with dominant acceptor properties, while the open symbols refer to donor solvents – the respective *DN* values are indicated inside each open circle. It will be seen that there is some relation between donor number and distance below the lines drawn to connect the non-donor solvent points. Although these figures give good qualitative support to the dual nature of solvent effects in these systems, it has not proved possible to establish a two-parameter equation of the type

$$\lambda_{max} = a(DN) + b(AN)$$

to give a satisfactorily quantitative fit to out present sets of data. The interaction of five-coordinate complexes with good donor solvents at the sixth coordination site, but with hydrogen-bonding solvents at a coordinated ligand, has previously been described for a number of vanadyl complexes [21].

There is one solvent whose effects do not seem to fit the general pattern of Figs. 4 and 5. The points for the strong donor solvent hexamethylphosphoramide, *HMPA*, do not appear at the expected level, *viz.* at the bottom of each figure. As *HMPA* is a particularly bulky solvent, there may well be steric hindrance to its approach to the manganese, which will lie significantly on the thiocyanate side of the plane defined by the four donor nitrogen atoms of the macrocycles. As the detailed geometry of the complexes $Mn(NCS)L^3$ and $Mn(NCS)L^5$ differs – in one case the ligand is planar, in the other it is saddle-shaped, and moreover the cavity sizes will be slightly different – it is difficult to provide a detailed explanation in the absence of full structural information from X-ray diffraction studies.

Figures 4 and 5 show that there are likely to be problems in correlating solvent effects on *charge-transfer* bands for these manganese complexes with data for other solvatochromic inorganic complexes. In particular, most of the information for the most studied complexes, $Fe(CN)_2(bipy)_2$ and $Fe(CN)_2(phen)_2$, has been obtained in solvents with strong or significant donor properties – which of course do not play

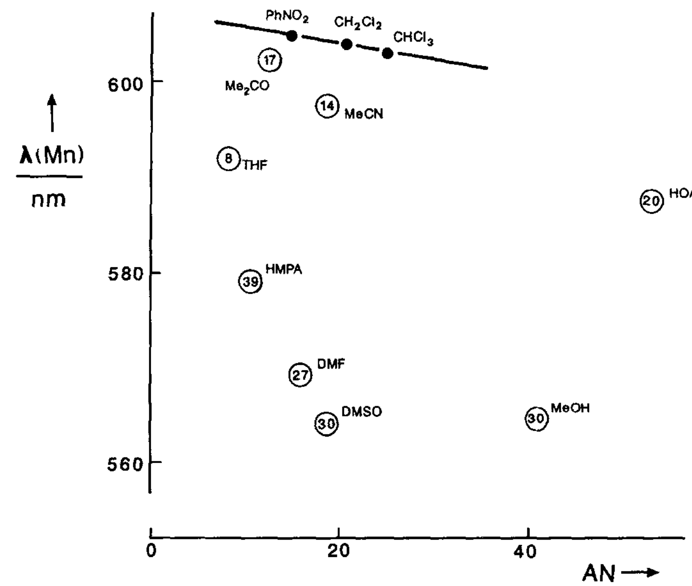


Fig. 4. Correlation of $\lambda(CT)$ for $Mn(NCS)L^3$ with solvent acceptor numbers (values in open circles are solvent donor numbers)

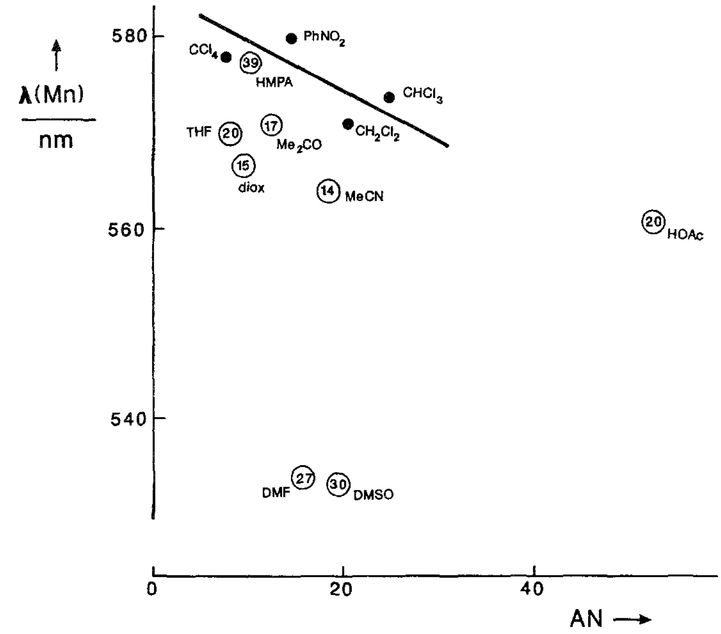


Fig. 5. Correlation of $\lambda(CT)$ for $Mn(NCS)L^5$ with solvent acceptor numbers (values in open circles are solvent donor numbers)

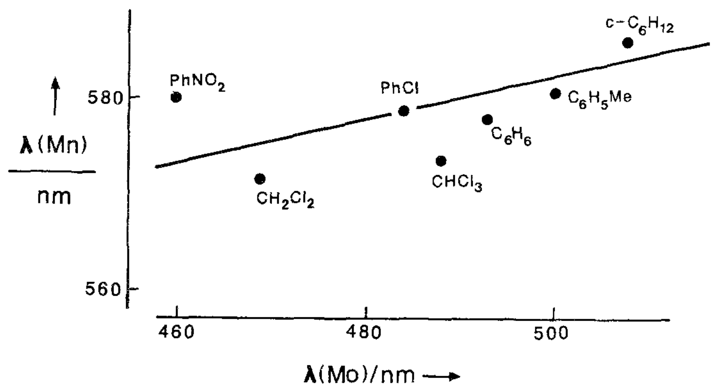


Fig. 6. Comparison of solvatochromism of $Mn(NCS)L^5$ with that of $Mo(CO)_4(bipy)$

an important role for these octahedral iron(II) species – due to solubility restrictions. However it has proved possible to compare solvent effects on the charge-transfer bands of $Mn(NCS)L^5$ and $Mo(CO)_4(bipy)$. Figure 6 shows that solvent effects, in non-donor solvents, are considerably smaller for the manganese compound. The solvent sensitivity of $Mn(NCS)L^5$ is only about 0.2 compared with that of the molybdenum compound.

The *charge-transfer* bands of solvatochromic inorganic complexes are also usually piezochromic, though pressure effects on λ_{max} are rather small – generally only a few nanometres for 1 kbar applied pressure [9, 10]. Pressure effects on the *charge-transfer* bands of $Mn(NCS)L^3$ and $Mn(NCS)L^5$ are reported in Table 2. The piezochromic coefficients $\partial v/\partial p$ have opposite signs in the two solvents. Presumably

Table 2. Pressure dependence of wavelengths of maximum absorption for the *charge-transfer* bands of thiocyanato-tetraaza-macrocycle-manganese complexes Mn(NCS)L

p/bar	$Mn(L^3)(NCS)$		$Mn(L^5)(NCS)$	
	Toluene	*DMF*	Toluene	*DMF*
1	592.5	569.5	579.0	534
250	594	569.5	580	533
500	594.5	568.5	582	532.5
750	595	568	582	532
1000	596	568.5	582.5	531.5
1250	596	568	582.5	
$\partial\nu/\partial p$[a]	−80	+60	−110	+90

[a] Units: $cm^{-1} kbar^{-1}$

in *DMF* we are monitoring the piezochromism of six-coordinate Mn(NCS)L(DMF), in toluene that of five-coordinate Mn(NCS)L. Molecular orbital energy levels and *charge-transfer* characteristics will therefore be different, so the resultant of pressure effects on the ground and excited states may well be opposite in sign. One might expect the direction of the solvatochromic shifts for the five and six coordinate species to differ, but it is not possible to establish solvatochromic behaviour for the *DMF* adduct. In the light of the previously established correlation between magnitudes of piezochromic and solvatochromic effects [22], we note here that the unusually small effects of pressure on *charge-transfer* bands for the five-coordinate species correspond with unusually low solvent sensitivity (*cf.* Fig. 6).

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