Transition Met. Chem., **24**, 355–361 (1999)

Structure, solvatochromism, and solvation of *trans*-[Co^{III}(cyclam)(NCS)$_2$](NCS) and the structure of [Co^{II}(Me$_4$cyclam)(NCS)]$_2$[Co(NCS)$_4$]MeOH

John Burgess, John Fawcett*, Robert I. Haines, Kuldip Singh and David R. Russell**
Chemistry Department, University of Leicester, Leicester LE1 7RH, UK

Summary

The structures of *trans*-[Co^{III}(cyclam)(NCS)$_2$](NCS) and of [Co^{II}(Me$_4$cyclam)(NCS)]$_2$[Co(NCS)$_4$]·MeOH have been established by X-ray diffraction methods. The solvatochromic behavior of the *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ cation in several binary aqueous solvent mixtures is reported. Transfer chemical potentials for this complex from H_2O into MeOH-H_2O mixtures have been established from solubility measurements on its thiocyanate salt. The solvatochromic behavior of this cation is discussed in the context of other solvatochromic inorganic complexes; its transfer chemical potentials are discussed in relation to those of other cobalt(III) complexes.

Introduction

Many years ago we discovered the complex *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$¶ to be solvatochromic(1,2). Whereas there are a large number of solvatochromic compounds and complexes of the *cis*-[ML$_4$L$'_2$], [M(LL)$_2$L$'$], or [ML$_4$(LL)] types, such as [Fe(diimine)$_2$(CN)$_2$], [Fe(diimine)(CN)$_4$]$^{2-}$, or [Mo(diimine)(CO$_4$)], where diimine = a (substituted) 2,2$'$-bipyridyl or 1,10-phenanthroline, a pyridine-derived Schiff base, or a diazabutadiene(3), there are very few reported solvatochromic *trans*-analogues. We have now completed a fuller investigation of the solvatochromism of *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ in water-rich binary aqueous solvent mixtures. We have confirmed the *trans*-geometry of the complexes by an X-ray diffraction crystal structure determination of its thiocyanate salt, improving on an earlier determination(1,4). We have also obtained complementary information on solvation of *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ by measuring solubilities of its thiocyanate and thence deriving transfer chemical potentials as a thermodynamic solvation indicator. We discuss the solvatochromism of *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ in relation to that of other inorganic complexes and compounds, especially ternary iron(II)-diimine-cyanide and molybdenum(0)-diimine-carbonyl species. We compare transfer chemical trends for *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ from water into methanol-water mixtures with trends established for a variety of cobalt(III) complexes and assess the effects of the cyclam and thiocyanate ligands on solvation in these binary media.

Our intended preparation of the analogous salt *trans*-[Co(Me$_4$cyclam)(NCS)$_2$]NCS), planned to provide a somewhat more hydrophobic complex cation, in fact produced the five-coordinated cobalt(II) complex [Co(Me$_4$cyclam)(NCS)]$^{+}$, in the form of a methanol solvate of its [Co^{II}(NCS)$_4$]$^{2-}$ salt. The structure of this salt has been established by X-ray diffraction methods, and is described hereunder. The solvatochromic behavior of the [Co(Me$_4$cyclam)(NCS)]$^{+}$ cation is, at any rate in water-rich mixed solvents, very similar to that of the *trans*-[Co(cyclam)(NCS)$_2$]$^{+}$ cation. Dissociation of the [Co^{II}(NCS)$_4$]$^{2-}$ anion on dissolving the salt in aqueous media prevented us from measuring solubilities and thence estimating transfer chemical potentials in methanol-water mixtures.

Experimental

Materials

The cobalt(III) salt *trans*-[Co(cyclam)(NCS)$_2$](NCS) was prepared by air oxidation of an aqueous solution of cobalt(II) chloride, cyclam, and a generous excess of sodium thiocyanate(5). An analogous experiment using Me$_4$cyclam in place of cyclam produced what proved to be the cobalt(II) salt [Co(Me$_4$cyclam)(NCS)]$_2$[Co(NCS)$_4$]·MeOH. The products were purified by recrystallisation from H_2O, to give deep orange-red (cyclam complex) or intensely blue (Me$_4$cyclam complex) crystals. The crystals used for the X-ray diffraction structure determinations were selected from the recrystallised products. The purity of the cyclam complex was checked through comparisons of its i.r. and uv-visible spectra with published data.

Doubly distilled H_2O was used for the solubility and spectroscopy experiments. The best commercially available grades of the organic cosolvents were used, some with further purification(6). Thus MeOH was allowed to stand over Mg turnings and a trace of I_2 before final distillation, and dioxan was passed down an alumina column to remove traces of peroxides before being distilled.

Spectroscopy and solubilities

Visible absorption spectra were run at 298 K in 1 cm cells in the thermostatted cell compartment of a Pye-Unicam SP8-100 or SP1800, a Shimadzu UV160, or a Perkin Elmer lambda 16 spectrophotometer. Solubilities were obtained by our usual method(7). It was checked that aquation was negligible over a period of several days at 298 K in the solvent media used for the solubility experiments.

X-ray structure determination

Details of X-ray data collection, and of solution and refinement of the structures(8), are summarised in

---

* Author to whom all correspondence should be directed.

** Present address: Department of Chemistry, University of Prince Edward Island, Charlottetown, P. E. I., Canada, C1A 4P3.

¶ cyclam = 1,4,8,11-tetraazacyclotetradecane;
Me$_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

Table 1. Crystal data, data collection and refinement parameters for *(1)* and *(2)*

Compound	*(1)*	*(2)*
Formula	$C_{12}H_{24}N_6S_2Co^+NCS^-$	$2(C_{15}H_{32}N_5SCo)^+Co(NSC)_4^{2-}.CH_4O$
Mol. Wt.	433.50	1070.18
Lattice	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
a Å	8.254(1)	8.630(2)
b Å	9.602(1)	23.930(7)
c Å	12.179(1)	24.419(5)
α°	90.87(1)	90
β°	92.20(1)	93.81(2)
γ°	90.23(1)	90
V $Å^3$, Z	964.4(2)	5032(2)
setting reflections, θ range(°)	37, 4.93–12.46	37, 5.11–12.44
crystal size mm	0.44 × 0.39 × 0.09	0.63 × 0.21 × 0.16
crystal colour/habit	orange plate	blue needle
Dx Mg m^{-3}	1.493	1.413
μ mm^{-1}	1.225	1.270
min., max. transmission	not applied	0.848, 0.964
scan range °	5.36–52	5.0–50
scan index limits (h, k, l)	−1 10, −11 11, −15 15	−1 10, −1 28, −29 28
data collected	4608	9750
unique data	3786	8557
goodness of fit on F^2	1.015	1.026
a,b[a] in weighting scheme	0.0361, 0.478	0.0359, 8.602
R (int)	0.0219	0.0558
observed data [$I > 2\sigma(I)$]	3086	4359
R1	0.0347	0.0717
wR2 (all data)	0.0898	0.1434
parameters n	220	526
ΔF e$Å^{-3}$	+0.374, −0.292	+0.787, −0.482
Δ/σ	0.001	0.000

$R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [w(Fo^2 - Fc^2)^2/(Fo^2)^2]^{1/2}$, goodness of fit $s = [\Sigma w(Fo^2 - Fc^2)^2/(n - p)]^{1/2}$ where n = number of reflections and p = total number of parameters, [a]$w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 - Fc^2)/3$.

Table 1. Atom numbering diagrams are shown as Figures 1 and 2; selected bond distances and bond angles are given in Tables 2, 3, and 4, for *trans*-[Co(cyclam)$(NCS)_2]^+$, [Co(Me_4cyclam)$(NCS)_2]^+$, and $[Co(NCS)_4]^{2-}$ respectively. All other crystallographic data may be obtained from the Cambridge Crystallographic Data Centre, where CIF files have been deposited {Deposition Number 102665 for *trans*-[Co(cyclam)$(NCS)_2$](NCS) *(1)* and Deposition Number 102666 for [Co(Me_4cyclam)(NCS)$]_2$[Co$(NCS)_4$} *(2)*.

Data for *(1)* and *(2)* were measured on a Siemens P4 diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) with an ω scan technique. 3 standard reflections monitored every 100 scans showed no significant variation in intensity, the reflections were corrected for Lorentz and polarisation effects. The structures were solved by Direct methods using the program SHELXTL-PC(8) and refined by full-matrix least squares on F^2. All hydrogen atoms were included in calculated positions (C—H = 0.96 Å) with isotropic displacement parameters set to $1.2U_{eq}(C)$. The methanol solvent molecule found in *(2)* was found to be disordered with two possible positions for the O atom (60:40), hydrogen atoms of the solvent molecule were not included in the refinement. All non-hydrogen atoms except the solvent methanol molecule of *(2)* were refined with anisotropic displacement parameters.

Results and discussion

Structures

The X-ray crystal structure determination for [Co(cyclam)$(NCS)_2$](NCS) *(1)* confirmed the *trans*-geometry originally assigned, on the basis of uv-visible spectro-

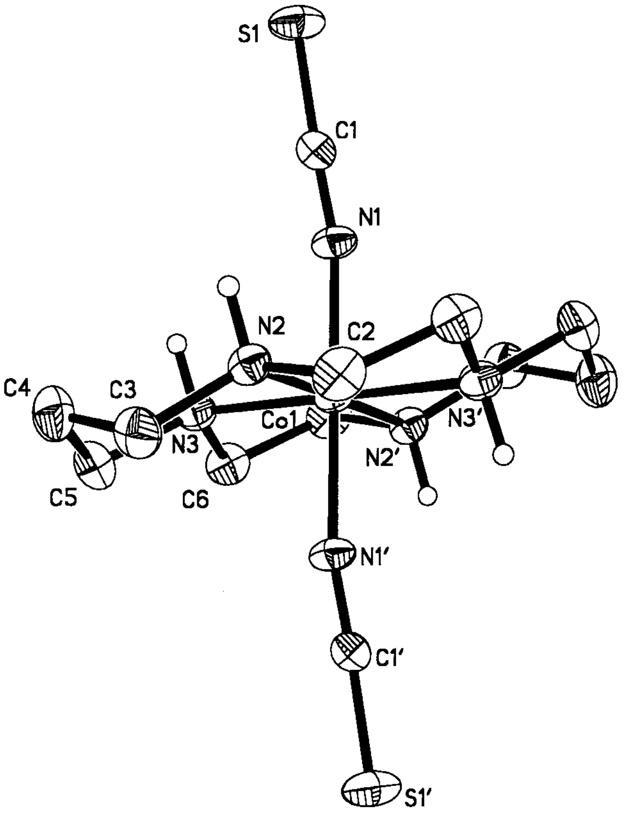
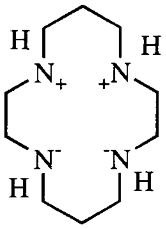


Figure 1. Structure of one of the unique cations of *(1)* showing the atom labelling scheme with 30% probability ellipsoids. H atoms except those bonded to N atoms are omitted for clarity. Primed atoms are generated by symmetry (code; 2−*x*, 1−*y*, *z*).

Table 2. Selected bond lengths (Å) and angles (°) for the *trans*-$[Co(cyclam)(NCS)_2]^+$ cation in *(1)*

Co(1)—N(1)	1.884(2)	Co(1)—N(2)	1.974(2)
Co(1)—N(3)	1.981(2)	S(1)—C(1)	1.609(3)
N(1)—C(1)	1.158(3)	Co(1A)—N(1A)	1.882(2)
Co(1A)—N(3A)	1.975(2)	Co(1A)—N(2A)	1.975(2)
S(1A)—C(1A)	1.612(3)	N(1A)—C(1A)	1.157(3)
N(1)—Co(1)—N(2)	88.85(10)	N(1)—Co(1)—N(3)	89.44(10)
N(2)—Co(1)—N(3)	93.70(9)	C(1)—N(1)—Co(1)	168.4(2)
N(1)—C(1)—S(1)	177.7(3)	N(1A)—Co(1A)—N(3A)	89.38(9)
N(1A)—Co(1A)—N(2A)	89.07(9)	N(3A)—Co(1A)—N(2A)	93.73(9)
C(1A)—N(1A)—Co(1A)	165.6(2)	N(1A)—C(1A)—S(1A)	179.0(2)

scopy (comparisons with spectra of *cis*- and *trans*-$[Co(LL)_2X_2]$)$^{(5)}$ for the $[Co(cyclam)(NCS)_2]^+$ cation. The thiocyanate-N—Co—thiocyanate-N angle is 180°, as it is in *trans*-$[Co(NH_3)_4(NCS)_2]^{+(9)}$. The conformation of the cyclam ligand is shown in (Figure 1), hydrogen atoms bonded to cyclam nitrogen atoms are included to indicate the conformation clearly. There are in principle several possible conformations for the cyclam, varying in stability over a range of 46 kJ mol$^{-1\,(10)}$. The conformation adopted here, that represented as *(3)* according to Curtis's convention$^{(11)}$, is the most stable – it is also that found in $[Ni(cyclam)Cl_2]^{(5,12)}$. Other features of this cation are mentioned in the general discussion below.



(3)

The central metal in the $[Co(Me_4cyclam)(NCS)]^+$ cation is five-coordinate. Structures of previously reported five-coordinate cobalt(II) complexes range from approximately trigonal bipyramidal to approximately square pyramidal$^{(13)}$. $[Co(Me_4cyclam)(NCS)]^+$ has a coordination geometry intermediate between the extremes of a square-based pyramid and a trigonal bipyramid. Appropriate N—Co—N angles are shown in the two representations of the CoN_5 core in Figure 3. The cation seems to be rather closer to a trigonal bipyramid, with the thiocyanate equatorial, than to a square-based pyramid.

The geometry of the central CoN_4 unit of $[Co(NCS)_4]^{2-}$ anion (all thiocyanates are N-bonded) is fairly close to tetrahedral, with angles ranging from 105.8 to 115.3°.

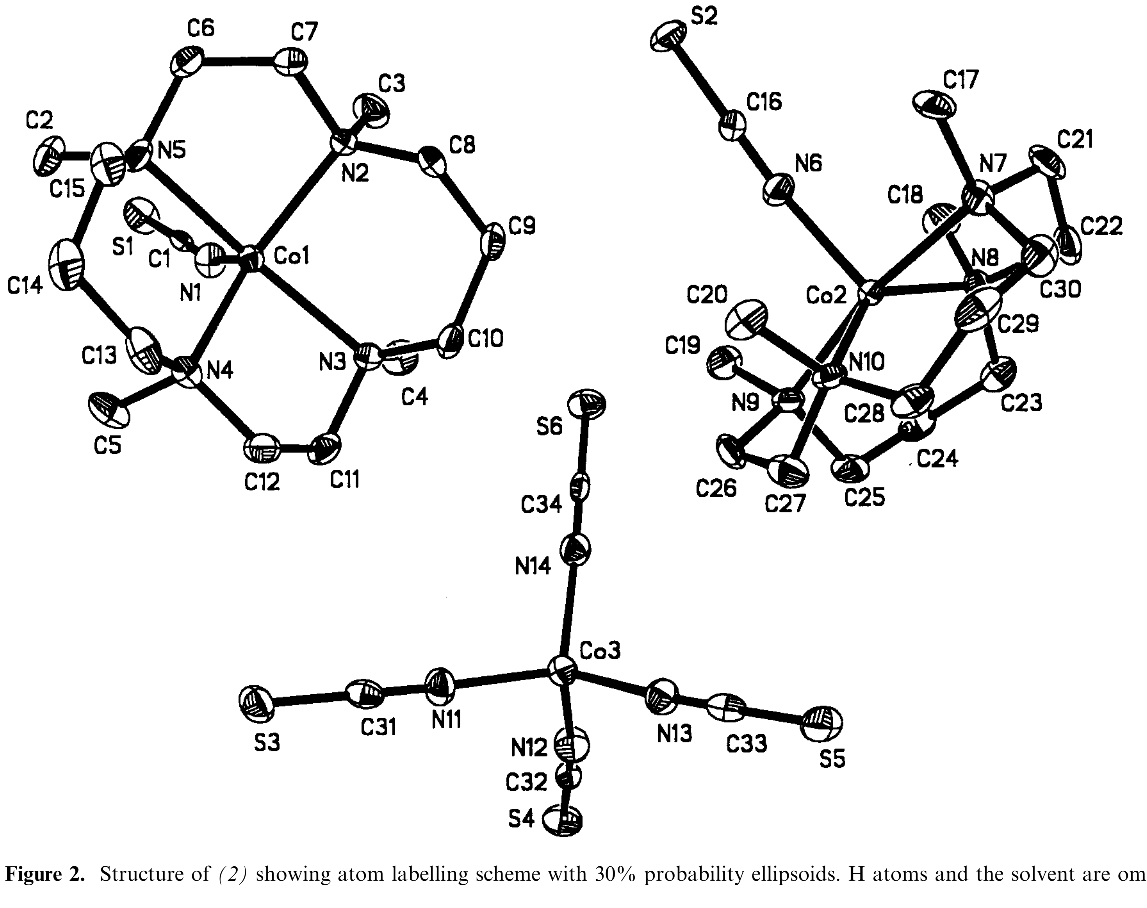


Figure 2. Structure of *(2)* showing atom labelling scheme with 30% probability ellipsoids. H atoms and the solvent are omitted for clarity.

Table 3. Selective bond lengths (Å) and angles (°) for the [Co(Me$_4$ cyclam)(NCS)]$^+$ cations in *(2)*

Co(1)—N(1)	1.966(7)	Co(1)—N(4)	2.092(6)
Co(1)—N(2)	2.110(6)	Co(1)—N(3)	2.207(6)
Co(1)—N(5)	2.213(6)	S(1)—C(1)	1.609(9)
N(1)—C(1)	1.165(9)	Co(2)—N(6)	1.971(7)
Co(2)—N(10)	2.115(6)	Co(2)—N(8)	2.123(6)
Co(2)—N(7)	2.194(6)	Co(2)—N(9)	2.204(6)
S(2)—C(16)	1.625(8)	N(6)—C(16)	1.151(9)
N(1)—Co(1)—N(4)	111.0(3)	N(1)—Co(1)—N(2)	108.9(3)
N(4)—Co(1)—N(2)	140.0(2)	N(1)—Co(1)—N(3)	96.3(3)
N(4)—Co(1)—N(3)	84.3(3)	N(2)—Co(1)—N(3)	92.6(2)
N(1)—Co(1)—N(5)	94.3(3)	N(4)—Co(1)—N(5)	92.5(3)
N(2)—Co(1)—N(5)	83.3(2)	N(3)—Co(1)—N(5)	169.4(2)
N(6)—Co(2)—N(10)	110.2(3)	N(6)—Co(2)—N(8)	108.1(3)
N(10)—Co(2)—N(8)	141.6(2)	N(6)—Co(2)—N(7)	94.6(3)
N(10)—Co(2)—N(7)	92.4(3)	N(8)—Co(2)—N(7)	83.8(2)
N(6)—Co(2)—N(9)	94.6(3)	N(10)—Co(2)—N(9)	84.6(2)
N(8)—Co(2)—N(9)	93.1(2)	N(7)—Co(2)—N(9)	170.9(2)

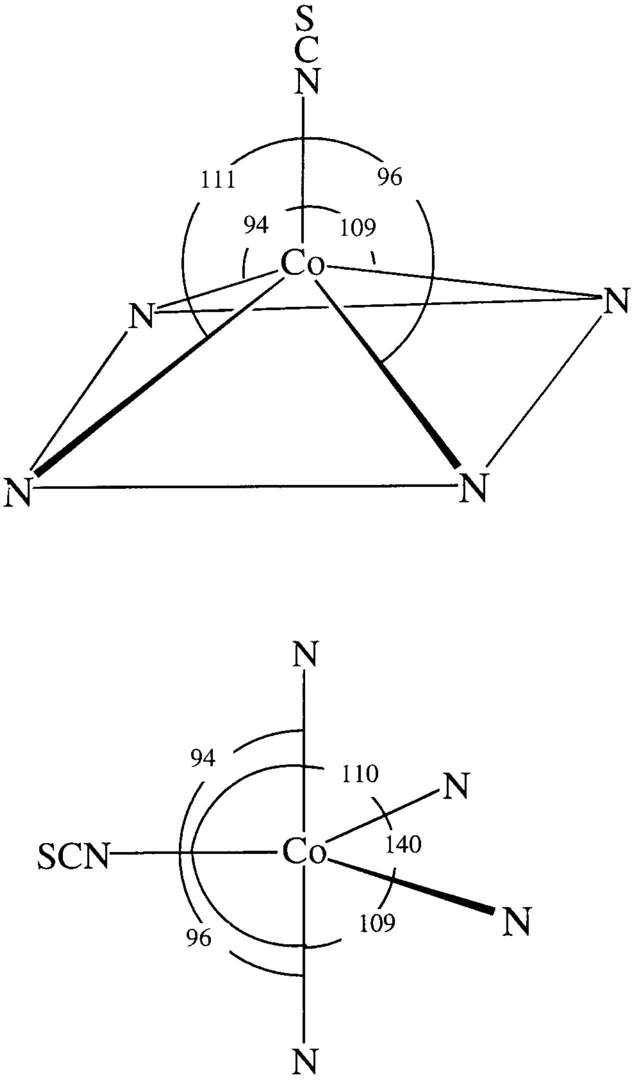


Figure 3. Relation of the coordination geometry around the cobalt in the *trans*-[Co(Me$_4$Cyclam)(NCS)]$^+$ cation to the square pyramidal and trigonal bipyramidal extremes for five-coordination.

Table 4. Selected bond lengths (Å) and angles (°) for the [Co(NCS)$_4$]$^{2-}$ anion in *(2)*

Co(3)—N(11)	1.944(7)	Co(3)—N(13)	1.946(7)
Co(3)—N(14)	1.951(7)	Co(3)—N(12)	1.955(7)
S(3)—C(31)	1.619(9)	N(11)—C(31)	1.161(10)
S(4)—C(32)	1.629(9)	N(12)—C(32)	1.144(9)
S(5)—C(33)	1.615(9)	N(13)—C(33)	1.158(10)
S(6)—C(34)	1.600(9)	N(14)—C(34)	1.178(9)
N(11)—Co(3)—N(13)	115.3(3)	N(11)—Co(3)—N(14)	108.6(3)
N(13)—Co(3)—N(14)	109.1(3)	N(11)—Co(3)—N(12)	107.4(3)
N(13)—Co(3)—N(12)	110.2(3)	N(14)—Co(3)—N(12)	105.8(3)
C(31)—N(11)—Co(3)	177.9(7)	N(11)—C(31)—S(3)	179.6(8)
C(32)—N(12)—Co(3)	168.7(8)	N(12)—C(32)—S(4)	178.2(8)
C(33)—N(13)—Co(3)	175.7(7)	N(13)—C(33)—S(5)	178.9(8)
C(34)—N(14)—Co(3)	167.2(7)	N(14)—C(34)—S(6)	179.6(7)

Cobalt-nitrogen distances, in the present complexes and for a selection of other cobalt complexes for comparison, are collected in Table 5$^{(9,13-23)}$. Cobalt-nitrogen distance to the macrocyclic ligands are in the expected ranges for cobalt(III) and cobalt(II) in the *trans*-[Co(cyclam)(NCS)$_2$]$^+$ and [Co(Me$_4$cyclam)(NCS)]$^+$ cations respectively. The difference between Co^{III}—N(thiocyanate) and Co^{II}—N(thiocyanate), in these and related complexes, is less marked. Cobalt(II)—nitrogen distances in the near-tetrahedral anion are all equal within experimental uncertainty. The mean value of 1.95 Å is the same, within experimental uncertainty, as the Co^{II}—N(thiocyanate) bond distance in the [Co(Me$_4$cyclam)(NCS)]$^+$ cation, but significantly less than in the six-coordinate complexes (Table 5).

The Co—N—C(thiocyanate) angles in a range of cobalt(II) and cobalt(III) thiocyanate complexes are listed in Table 5. There is a remarkable range of values, with the Co—N—C angles indicating deviations from linearity of from 2 to 35°. These angles in *trans*-[Co(cyclam)(NCS)$_2$]$^+$ are 166 and 168°, deviating significantly more from linearity than the Co—N—C angles of 176° in the analogous ammine complex. The angle in [Co(Me$_4$cyclam)(NCS)]$^+$ is, at 164°, very similar. It is in the homoleptic cobalt(II) anions [Co(NCS)$_4$]$^{2-}$ and [Co(NCS)$_6$]$^{4-}$ that the biggest and smallest deviations occur, with the shapes of the former in the two salts of established structure being markedly different. Inclusion of iodoform of crystallisation also has a considerable effect on thiocyanate geometry in the ternary complexes with pyridine$^{(24,25)}$d (Table 6).

Solvatochromism

The band at 524 nm (in water) for *trans*-[Co(cyclam)(NCS)$_2$]$^+$ shifts slightly but progressively to longer wavelength (lower energy) as the proportion of organic cosolvent increases (Table 7). This behaviour parallels that of the MLCT bands of complexes of the iron(II)-diimine-cyanide type, but the shifts for the cobalt complex are much less than those for the iron(II) complexes. Plots of shifts for the *trans*-[Co(cyclam)(NCS)$_2$]$^+$ cation against those for [Fe(bipy)$_2$(CN)$_2$], the reference iron(II)-diimine-cyanide complex, for water-methanol and water-ethanol mixtures give a reasonable correlation, with a slope 0.27; points for i-propanol and for dioxan as cosolvents lie appreciably off this correlation line. As so often is the case for inorganic substrates, shifts for *trans*-[Co(cyclam)(NCS)$_2$]$^+$ correlate less well with solvent E$_T$ values$^{(26)}$, the standard organic solvatochromism reference scale.

Inspection of Table 7 shows that [Co(Me$_4$cyclam)(NCS)]$^+$ exhibits similar solvatochromic beha-

Table 5. Cobalt—nitrogen bond distances (Å) in *trans*-$[Co(cyclam)(NCS)_2]^+$, $[Co(Me_4cyclam)(NCS)]^+$, and $[Co(NCS)_4]^{2-}$, with some comparative data

	Co—N[am(m)ine]^a	Co—N(thiocyanate)	Ref.
Cobalt(II) Complexes			
Four-Coordinate			
$[Co(NCS)_4]^{2-}$		1.95	b; 14
Five-Coordinate			
$[Co(Me_4cyclam)(NCS)]^+$	2.09 to 2.21	1.97	b
$[Co(Me_6tren)Br]^+$	2.08 to 2.15		13
Six-Coordinate			
$[Co(NH_3)_6]^{2+}$	2.16		15
cis-$[Co(bipy)_2(NCS)_2]$	2.15 to 2.19	2.06, 2.08	16
trans-$[Co(X\text{-}py)_4(NCS)_2]^c$	2.15 to 2.20	2.05 to 2.10	17–19
trans-$[Co(mbtz)_4(NCS)_2]^d$	2.21	2.05	20
$[Co(NCS)_6]^{2-}$		2.11 to 2.14	21
Cobalt(III) Complexes			
trans-$[Co(cyclam)(NCS)_2]^+$	1.98	1.88	b
trans-$[Co(NH_3)_4(NCS)_2]^+$	1.96	1.91	9
cis-$[Co(tn)_2(NCS)_2]^{+e}$	1.99	1.92	22
$[Co(NH_3)_5(NCS)]^{2+}$	f	1.90	23
$[Co(NH_3)_6]^{3+}$	1.97		15

[a] Or pyridine. [b] This work. [c] X = H, 4-benzoyl, or 4-vinyl (orthorhombic and tetragonal forms). [d] mbtz = 1-methylbenzotriazole. [e] tn = 1,3-propanediamine (trimethylenediamine). [f] Not reported (disorder problems).

Table 6. Co—N—C angles at coordinated nitrogen of thiocyanate in cobalt(II) and cobalt(III) complexes

Complex	Co—N—C angle	Ref.
Cobalt(II) Complexes		
$[Co(NCS)_4]^{2-}$	156 to 178° ^{a}	b, 14
trans-$[Co(py)_4(NCS)_2]$	155.9°	17
trans-$[Co(py)_4(NCS)_2]2CHI_3$	174.7°	23
trans-$[Co(py)_4(NCS.I_2)_2]$	177.3°	24
trans-$[Co(4\text{-benzoyl py})_4(NCS)_2]$	173.8°	19
$[Co(Me_4cyclam)(NCS)]^+$	164°	b
Cobalt(III) Complexes		
$[Co(NCS)_6]^{2-}$	145 to 165°	21
trans-$[Co(cyclam)(NCS)_2]^+$	166 to 168°	b
trans-$[Co(NH_3)_4(NCS)_2]^+$	176°	9
cis-$[Co(tn)_2(NCS)_2]^+$	166 to 173°	22

[a] 167 to 178° in the nitron salt, 156 to 175° in the $[Co(Me_4cyclam)(NCS)]^+$ salt. [b] This work.

Table 7. Wavelengths (nm) of maximum absorption for *trans*-$[Co(cyclam)(NCS)_2]^+$ and for $[Co(Me_4cyclam)(NCS)]^+$ in binary aqueous solvent mixtures

Cosolvent (vol %)	20	40	60	80	90
trans-$[Co(cyclam)(NCS)_2]^{+a}$					
MeOH	527	528	529	532	535
EtOH	528	529	531	533	535
i-PrOH	525	526	528	529	
1,4-dioxan	526	527	530	532	535
Me_2Co	525	527	529	531	
$[Co(Me_4cyclam)(NCS)]^{+b}$					
MeOH	481 (708)^c	482 (710)^c	484 (712)^c		

[a] 524 nm in H_2O. [b] 480 (706) nm in H_2O. [c] Broad weak band.

Table 8. Solubilities (at 298.2 K) of *trans*-$[Co(cyclam)(NCS)_2](NCS)$ and derivation of transfer chemical potentials for *trans*-$[Co(cyclam)\text{-}NCS)_2]^+$

MeOH (vol %)	0	10	20	30	40
ASS^a	2.70^b	1.99	1.73	1.60	1.68
ΔG_{tr}(salt)/kJ mol^{-1}		+1.5	+2.2	+2.6	+2.4
$\Delta G_{tr}(NCS^-)$/kJ mol^{-1} ^{c}		−0.2	−0.3	−0.3	−1.4
ΔG_{tr}(complex)/kJ mol^{-1}		+1.7	+2.5	+2.9	+2.8

[a] Absorbance of saturated solution, measured at λ_{max}. [b] This corresponds to a solubility of 0.010 mol dm^{-3} (ε_{524} = 270, according to Figure 3 of reference 5) [c] Mean values estimated as detailed in the text.

viour to *trans*-$[Co(cyclam)(NCS)_2]^+$. The shifts are too small to make a quantitative comparison, but the shifts are, as one would expect, in the same direction and are perhaps slightly smaller than for the Me_4cyclam complex. The presence of a formally vacant sixth coordination site in the Me_4cyclam complex might lead one to expect greater sensitivity to solvent composition. Either this site has a strong preference for water, or it is sufficiently well shielded by the bulky ligand that solvation at this site is not significant. An earlier study of solvatochromism of five-coordinate manganese(III)-tetraazamacrocycle-thiocyanate complexes showed similarly low solvent sensitivities, but did indicate significant solute–solvent interactions in strong donor solvents. We cannot make direct comparisons between $[Co(Me_4cyclam)(NCS)]^+$ and the manganese systems, since the latter were studied in a range of non-aqueous solvents, the former in water-rich mixtures.

Transfer chemical potentials

The derivation of transfer chemical potentials for the *trans*-$[Co(cyclam)(NCS)_2]^+$ cation is set out in Table 8. The single ion assumption employed is the TATB (or TPTB; the difference is < 1% over our range of solvent mixtures) assumption, i.e. it is assumed that transfer chemical potentials for the large and lightly solvated tetraphenylarsonium (TA, or tetraphenylphosphonium, TP) cation and tetraphenylboronate (TB) anion are equal. This assumption enters the calculations via the published data used for the transfer chemical potentials for thiocyanate. There are three sets of these values, based on Gibbs energies of transfer of $H^+ + NCS^-$(27), on solubilities of the thiocyanate and perchlorate of the $[Co(en)_2(ox)]^+$ cation(28), and on solubilities of a range of thiocyanate and perchlorate salts of iron(II)-diimine cations(1). The last two are in turn based on published transfer chemical potentials for perchlorate. The values

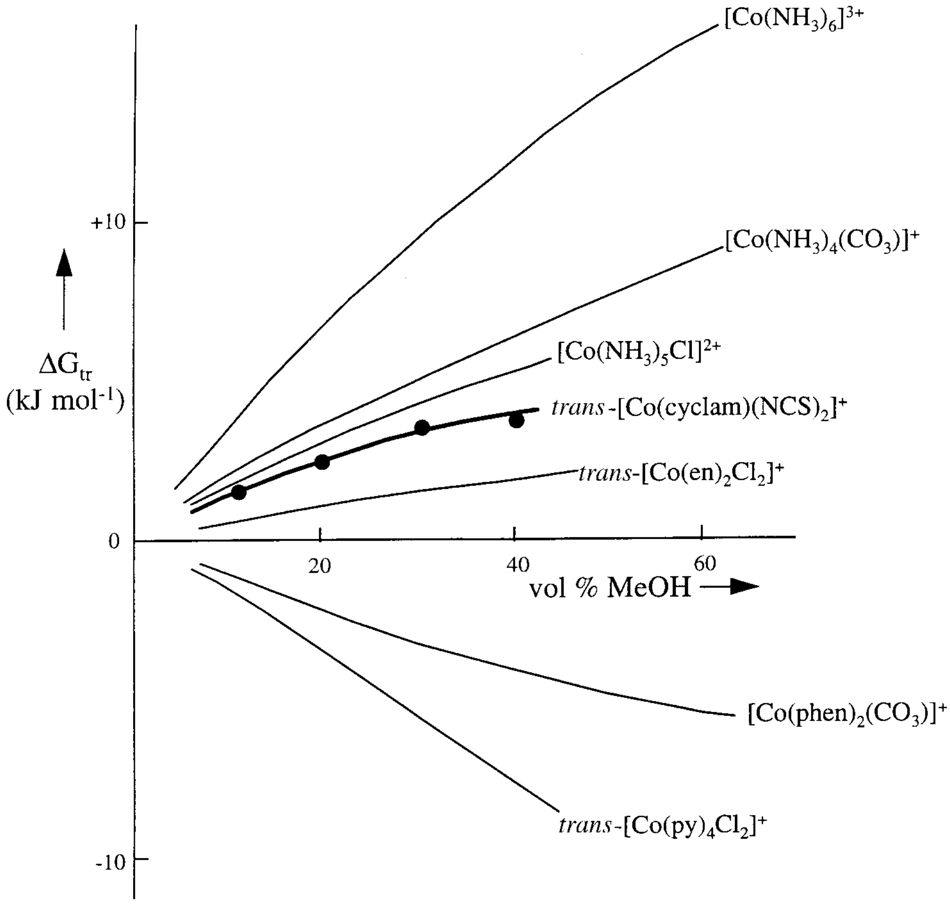


Figure 4. Transfer chemical potentials for *trans*-$[Co(Cyclam)(NCS)_2]^+$ and a selection of other cobalt(III) complexes from water into aqueous methanol (at 298 K).

from the three sets agree well, within about 1 kJ mol^{-1} over the solvent composition range 0 to 40% methanol, so we have averaged the three sets for use in Table 8. The derived transfer chemical potentials for *trans*-$[Co(cyclam)(NCS)_2]^+$ from water into water-rich methanol-water mixtures are slightly but significantly positive. Such modestly unfavourable transfer from water into the mixed solvents indicates that the complex shows a slight preference for solvation by water. The hydrophilic thiocyanates and the charge on the complex are just outweighing the hydrophobic periphery of the coordinated cyclam.

The transfer chemical potential trend for *trans*-$[Co(cyclam)(NCS)_2]^+$ is compared with trends for a selection of other cobalt(III) complexes(29) in Figure 4. This Figure shows how relatively small the transfer chemical potentials are for this complex, especially in comparison with, on the one hand, the strongly hydrophilic $[Co(NH_3)_6]^{3+}$ and, on the other, $[Co(phen)_2(CO_3)]^+$ and *trans*-$[Co(py)_4Cl_2]^+$. In the case of these latter complexes, the strongly hydrophobic characters of the coordinated 1,10-phenanthroline or pyridine ligands dominate over the effects of the hydrophilic carbonate or chlorides.

We were not able to determine transfer chemical potentials from solubilities for the $[Co(Me_4cyclam)(NCS)]^+$ cation. In the first place, there are no transfer chemical potentials published for the $[Co(NCS)_4]^{2-}$ anion, and in the second place, this anion dissociates into Co^{2+}aq and NCS^- on dissolution in water, as is evidenced by the pale pink colour (and the spectrum) of the aqueous supernatant above solid $[Co(Me_4cyclam)(NCS)]_2[Co(NCS)_4]$*(2)*.

Acknowledgement

We wish to acknowledge the use of EPSRC's Chemical Database Service at Daresbury(30).

References

(1) R. I. Haines, *Ph.D. thesis*, Leicester, 1977.
(2) J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem.*, **6**, 145 (1981).
(3) E. g., M. Kotowski, R. van Eldik, Razak bin Ali, J. Burgess and S. Radulovic, *Inorg. chim. Acta*, **131**, 225 (1987); Razak bin Ali, J. Burgess, M. Kotowski and R. van Eldik, *Transition Met. Chem.*, **12**, 230 (1987); and refs therein.
(4) J. Burgess, R. I. Haines, D. R. Russell and W. Scutcher, unpublished.
(5) B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
(6) A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York, 1972, pp. 429–437.
(7) M. J. Blandamer, J. Burgess, B. Clark, P.P. Duce, A. W. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. D. Hubbard and E. A. Abu-Gharib, *J. Chem. Soc.*, *Faraday Trans.I*, **82**, 1471 (1986).
(8) G. M. Sheldrick, SHELXTL-pc Release 4.2, Siemens Analytical X-ray Instruments, Madison, WI, 1991
(9) T. J. Westcott, A. H. White and A. C. Willis, *Aust. J. chem.*, **33**, 1853 (1980).
(10) See, e.g., M. L. Tobe and J. Burgess, *Inorganic Reaction Mechanisms*, Addison-Wesley-Longman, Harlow, 1999, Chs. 4.5.3.

(11) P. O. Whimp, M. F. Bailey and N. F. Curtis, *J. Chem. Soc. (A)*, 1956 (1970).

(12) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(13) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967).

(14) S. Cerrini, M. Colapietro, R. Spagna, and L. Zambonelli, *J. Chem. Soc. (A)*, 1375 (1971).

(15) B. S. Brunschwig, C. Creutz, D. H. Macartney, T.-K Sham and N. Sutin, *Faraday Disc. Chem. Soc.*, **74**, 113 (1982); and refs therein.

(16) M. V. Veidis, B. Dockum, F. F. Charron, W. M. Reiff and T. F. Brennan, *Inorg. Chim. Acta*, **53**, L197 (1981).

(17) H. Hartl and I. Brudgam, *Acta Crystallogr. Sect. B*, **36**, 162 (1980).

(18) G. D. Andreetti and P. Sgarabotto, *Cryst. Struct. Commun.*, **1**, 55 (1972); B. M. Foxman and H. Mazurek, *Inorg. Chim. Acta*, **59**, 231 (1982).

(19) M. G. B. Drew, N. I. Gray, M. F. Cabral and J. de O. Cabral, *Acta Crystallogr. Sect. C*, **41**, 1434 (1985).

(20) J. C. Plakatouras, S. P. Perlepes, D. Mentzafos, A. Terzis and V. Papaefthymiou, *Polyhedron*, **11**, 2657 (1992).

(21) T. N. Mali, R. D. Hancock, J. C. A. Boeyens and E. L. Oosthuizen, *J. Chem. Soc., Dalton Trans.*, 1161 (1991).

(22) K. Matsumoto, S. Ooi, H. Kawaguchi, M. Nakano and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **55**, 1840 (1982).

(23) M. R. Snow and R. F Boomsma, *Acta Crystallogr. Sect. B*, **28**, 1908 (1972).

(24) H. Hartl and S. Steidl, *Acta Crystallogr*, **B36**, 65 (1980).

(25) H. Hartl and S. Steidl, *Z. Naturforsch.*, **32B**, 6 (1977).

(26) K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann, Chem.*, **661**, 1 (1963); C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, **4**, 29 (1965); C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, **18**, 98 (1979); C. Reichardt and E. Harbusch-Görnert, *Liebigs Ann. Chem.*, 721 (1983).

(27) C. Patra and P. K. Das, *Thermochimica Acta*, **53**, 357 (1982); M. H. Abraham, T. Hill, H. C. Ling, R. A. Schultz and R. A. C. Watt, *J. Chem. Soc., Faraday Trans. 1*, **80**, 489 (1984).

(28) M. J. Blandamer, J. Burgess and E. A. Abu-Gharib, *Transition Met. Chem.*, **9**, 193 (1984); J. Burgees and E. A. Abu-Gharib, *Transition Met. Chem.*, **9**, 234 (1984).

(29) M. J. Blandamer and J. Burgess, *Transition Met. Chem.*, **13**, 1 (1988).

(30) The United Kingdom Chemical Database Service: D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, **36**, 746 (1996).

(Received 17 September 1998;
Accepted 7 October 1998) TMC 4350