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Amine–Thiocyanates of Vanadium(II)

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Complexes of vanadium(II) thiocyanate with pyridine (py), 3- and 4-methylpyridine (3-mepy and 4-mepy respectively), 4-cyanopyridine (CN-py), 1,10-phenanthroline (phen), and 2,2'-bipyridyl (bipy) have been isolated from aqueous ethanol under nitrogen. Infrared spectra show that [V(py)$_4$(NCS)$_2$], [V(3-mepy)$_4$(NCS)$_2$], and [V(4-mepy)$_4$(NCS)$_2$] contain trans*-N-bonded anions but [V(phen)$_2$(NCS)$_2$] and [V(bipy)$_2$(NCS)$_2$] contain* cis*-N-bonded anions. The complexes are magnetically-dilute with essentially temperature-invariant magnetic moments slightly less than 3.87 B.M. The complexes [V(py)$_4$(NCS)$_2$] and [Ni(py)$_4$(NCS)$_2$] have similar powder photographs, as have [V(phen)$_2$(NCS)$_2$] and [Cr(phen)$_2$(NCS)$_2$].*

Introduction

Complexes of vanadium(II) halides with mono- and bi-dentate heterocyclic amines have recently [1, 2] been investigated. Single crystal investigations have shown [3] that [V(pyridine)$_4$Cl$_2$] has a *trans*-structure, and the structure of tris[dihydrobis(1-pyrazolyl)borato]vanadate(II) has been described [4]. This paper reports [5] the preparation and properties of some amine-thiocyanates of vanadium(II), *i.e.,* [V(amine)$_4$(NCS)$_2$] where the amine is pyridine (py), 3-methylpyridine (3-mepy), 4-methylpyridine (4-mepy), or 4-cyanopyridine (CNpy); and [V(amine)$_2$(NCS)$_2$] in which the amine is 1,10-phenanthroline (phen) or 2,2'-bipyridyl (bipy). The only other known thiocyanates of vanadium(II) are [6] [VL$_4$(NCS)$_2$]$_2$ where L = N-methylimidazole or 1,2-dimethylimidazole, and the hexaisothiocyanates K$_4$[V(NCS)$_6$] [7] and A$_4$[V(NCS)$_6$] [5], where A = substituted ammonium cation.

Experimental

To prepare the complexes (Table I) a solution containing vanadium(II) thiocyanate was first prepared by the addition of aqueous ammonium thiocyanate in 2:1 molar ratio to aqueous vanadium(II) bromide [8]. Attempts to isolate solid vanadium(II) thiocyanate by concentration of the solution gave a green solid of uncertain composition so the complexes were crystallised by the addition of the aqueous mixture to stoicheiometric amounts of the appropriate amine dissolved in 20% ethanol. The complexes were filtered off, washed with water and ethanol, and dried *in vacuo.* With 4-cyanopyridine warm 20% ethanol was used to dissolve the ligand, and the complex crystallised on cooling. The complexes slowly changed colour through oxidation on exposure to air. They were insoluble in water, but more soluble in ethanol and acetone.

Attempts to prepare bis(amine) complexes by using 2:1 pyridine-to-metal ratios were unsuccessful; the tetrakis(amine) complex always separated. No complexes of 2-methylpyridine could be isolated, presumably due to steric hindrance.

The complexes were analysed for vanadium either by ignition to V$_2$O$_5$ at 800 °C, after treatment with a few drops of concentrated sulphuric and nitric acids and careful heating to dryness; or by atomic absorption (Perkin Elmer P.E. 306 Spectrometer) with an air/acetylene reducing flame. The complexes were digested in concentrated sulphuric and nitric acids before appropriate dilution. The instrument was calibrated with standard vanadium solutions supplied by B.D.H. Ltd.

Magnetic measurements were carried out by the Gouy method on apparatus supplied by Newport Instruments, and calibrated with Hg[Co(NCS)$_4$]. Diffuse reflectance spectra of samples in sealed cells were recorded on a Unicam SP 700C spectrophotometer provided with a SP 735 diffuse-reflectance attachment and a lithium fluoride reference. Mulls for i.r. spectra were prepared in a nitrogen-filled glove bag, and recorded on a Perkin Elmer 577 spectrophotometer over the range 4000–200 cm^{-1}. X-ray powder photographs were taken with a Philips Debye-Scherrer camera, type P.W. 1026, of diameter 114.6 mm mounted on a Philips X-ray generator. Copper K$_\alpha$ radiation was used with a nickel filter. The samples were sealed in Lindemann capillaries, or thin-walled glass capillaries.

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TABLE I. Analyses and Magnetic Data.

Complex	Colour	C[a]	H	N	V	T/K	μ_{eff}[b]/B.M.	θ[b]/°	10^6 × Diamagnetic correction/$cm^3\ mol^{-1}$
$[V(py)_4(NCS)_2]$	dark brown	54.1(54.9)	4.1(4.2)	17.4(17.5)	10.5(10.6)	295 90	3.83 3.86	0	−258
$[V(4\text{-mepy})_4(NCS)_2]$	dark brown	58.2(57.9)	5.3(5.2)	15.2(15.6)	9.5(9.4)	295 90	3.70 3.67	0	−318
$[V(3\text{-mepy})_4(NCS)_2]$	dark brown	57.6(57.9)	5.1(5.2)	15.2(15.6)	9.7(9.4)	295 90	3.82 3.79	0	−318
$[V(CNpy)_4(NCS)_2]$	dark blue	52.75(53.5)	2.5(2.8)	24.1(24.0)	8.7(8.7)	295 90	3.82 3.69	7	−307
$[V(bipy)_2(NCS)_2]\cdot H_2O$	dark blue	53.6(53.1)	3.2(3.6)	16.8(16.9)	10.0(10.2)	295 90	3.86 3.75	7	−285
$[V(phen)_2(NCS)_2]$	dark green	58.2(59.2)	3.1(3.1)	15.7(15.9)	9.5(9.7)	295 90	3.72 3.63	4	−318

[a] Calculated percentages in parentheses. [b] Calculated from $\mu_{eff} = 2.828\,(\chi_A T)^{1/2}$ and the Curie–Weiss law, $\chi_A^{-1} \propto (T + \theta)$.

TABLE II. Thiocyanate[a] Absorption Bands and Reflectance Spectra.

	ν(CN)	ν(CS)	2δ(NCS)	δ(NCS)	ν(V–NCS)	ν(V–py)	Reflectance Spectra (cm^{-1})[b]				
$[V(py)_4(NCS)_2]$	2070vs, sp	805m	970vw[c] 960vw	490m 485m	343vs	281s	38000s	32000s	20500s, vb	15500sh	
$[V(4\text{-mepy})_4(NCS)_2]$	2060vs, sp	815sh[c] 808m	966w, b[c]	490m[c]	330s	300s 290sh	38800s	32000s	20000s, vb	16500sh	9000w
$[V(3\text{-mepy})_4(NCS)_2]$	2063vs, sp	818m, 805sh[c] 798s, 792s	980w[c] 963w	496w[c] 486m	326s, b	275s, b	36700sh	31500s	20500s, vb	17500sh	
$[V(CNpy)_4(NCS)_2]$	2040vs[d]	820s[c] 778m[c]	962m 955sh	485m	340s 320m	280m			23000vs, vb		
$[V(bipy)_2(NCS)_2]\cdot H_2O$	2066sh 2060vs	810w	970m, b[c]	489w	380sh 355s	–	38000s	30000sh	26500s, b	14000vs, b	
$[V(phen)_2(NCS)_2]$	2070sh 2063vs	811w	975w 955w	489w	350sh, 330m, b 315sh	–	34500s, b	31000sh	21500sb	13500vs, b	

[a] N-Bonded thiocyanate absorbs (ref. 5) in the following approximate ranges (cm^{-1}): ν(CN), 2120–2050; ν(CS), 860–780; δ(NCS), 490–450. [b] At room temperature; there were only minor changes on cooling to liquid nitrogen temperature. [c] Assignments have been made by comparison with the spectra of the corresponding halides where these are known (ref. 1), but in these regions ligand absorptions make assignments uncertain. [d] ν(CN) of 4-cyanopyridine at 2214 cm^{-1}.

TABLE III. X-Ray Powder Data[a] (*d* spacings, Å).

$[V(py)_4(NCS)_2]$	$[Ni(py)_4(NCS)_2]$	$[V(phen)_2(NCS)_2]$	$[Cr(phen)_2(NCS)_2]$
8.21vs	8.10vs	8.54s	8.34s
7.61s	7.12s	7.80s	7.88s
	6.72s	7.08s	7.19s
5.92vw	5.83w	6.40vw	6.37vw
5.40vw	5.37w	5.79m	5.75w
4.64m	4.77w	5.00m	5.13w
4.50m		4.59s	4.59s
4.34vs	4.33vs	3.75vs	3.78vs
4.02s	4.00vs		3.65m
3.83s	3.80vs	3.25m	3.26vw
3.68s		3.16m	3.18vw
3.58m	3.56vs	3.02w	3.04w

[a] Estimated visual intensities.

Results and Discussion

The effective magnetic moments μ_{eff} (Table I) are slightly below the spin-only value of 3.87 B.M. and essentially independent of temperature as expected for a d^3 metal ion in magnetically-dilute complexes. This confirms the oxidation state of the metal ions.

The ambidentate nature of the thiocyanate ion is well-known, but the infrared bands of the thiocyanate groups (Table II) establish [9] that N-bonded anions are present. Additionally, the CN stretching absorptions for the tetrakis(pyridine) complexes are intense and very sharp, indicative of *trans*-structures as found [3] for $[V(py)_4Cl_2]$ whereas the complexes $[V(bipy)_2(NCS)_2]$ and $[V(phen)_2(NCS)_2]$ exhibit split CN stretching absorptions suggestive of *cis*-structures. It is possible that solid state effects rather than stereochemical differences are responsible for the splittings particularly as there are three NCS deformations in one spectrum. However, the splittings (~7 cm^{-1}) are of the same order as in [11] the spectra of *cis*-$[Fe(phen)_2(NCS)_2]$ (12 cm^{-1}) and *cis*-$[Cr(phen)_2(NCS)_2]$ (16 cm^{-1}). In addition, *cis*-$[Cr(phen)_2(NCS)_2]$ and $[V(phen)_2(NCS)_2]$ have similar powder patterns (Table III). The ν(M–NCS) and ν(M–py) vibrations are at higher frequency than in corresponding complexes of metals later in the first transition series [10].

As with [1] the pyridine-halides, $[V(py)_4X_2]$, in which X is Cl, Br or I, the electronic spectra of the isothiocyanato-complexes are dominated by charge transfer absorptions down to approximately 16000 cm^{-1}. The low frequency, anion-dependent bands or shoulders visible in the spectra of most compounds of the type $[V(py)_4X_2]$ and assigned to the ${}^4B_{1g} \rightarrow {}^4E_g^a$ and ${}^4B_{1g} \rightarrow {}^4B_{2g}$ transitions in D_{4h} symmetry are absent. This would be expected as co-ordination of N-bonded thiocyanate would reduce the distortion and move the ${}^4A_{2g} \rightarrow {}^4T_g(\nu_1)$ transition (O_h symmetry) to higher frequency. It is possible that the shoulders in the spectra of the pyridine and methylpyridine thiocyanates near 16000 cm^{-1} (Table II) correspond to the ν_1 transition since in $[V(ethylenediamine)_3]X_2$ and related compounds [1] with saturated N-donor ligands ν_1 occurs at slightly lower frequencies.

X-Ray crystallographic investigations [12] have shown that the complex $[Ni(py)_4(NCS)_2]$ has a *trans*-structure with N-bonded thiocyanate. The Ni–N bond distances are Ni–NCS, 2.12 Å, and Ni–py, 2.03 Å and the Ni–NCS angle approximately 165°. This complex and $[V(py)_4(NCS)_2]$ have similar powder patterns (Table III) thus confirming the *trans*-structure of the latter. From their powder patterns $[Cr(phen)_2(NCS)_2]$, which is also believed [13] to have a *cis*-structure, and $[V(phen)_2(NCS)_2]$ are isomorphous. The corresponding bipyridyl complexes have somewhat different powder patterns.

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