Hexaisothiocyanates of Vanadium(II)

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Infrared spectra show that the new vanadium(II) complexes $[\text{cation}]_4[V(NCS)_6]$, where cation = NMe_4^+, NEt_4^+, Hpy^+, or $Hhex^+$ [py = pyridine, hex = hexamine (hexamethylenetetramine)], contain *N*-bonded thiocyanate, and the V–NCS stretching vibrations are at considerably higher frequencies than for corresponding complexes of later metals of the first transition series. The frequencies of the lowest-energy *d–d* band confirm that *N*-bonded thiocyanate is present. The complexes obey the Curie law, and $[NEt_4]_4[V(NCS)_6]$ is isomorphous with the analogous nickel(II) salt.

MANY thiocyanato-complexes of transition metals have been isolated,[1] but few of bivalent vanadium are known. The recent characterisation [2] of potassium hexaisothiocyanatovanadate(II), $K_4[V(NCS)_6]\cdot C_2H_5OH$, leads us to report [3] that we have isolated the salts $[\text{cation}]_4[V(NCS)_6]$, where cation = NMe_4^+ NEt_4^+, Hpy^+, or $Hhex^+$ {py = pyridine and hex = hexamine (1,3,5,7-tetra-azatricyclo[3.3.1.1^{3,7}]decane)}. Some amine-thiocyanates of vanadium(II) are known, *i.e.* $[VL_4(NCS)_2]$ (where L = a substituted imidazole [4] or a substituted pyridine [5]) and $[VL_2(NCS)_2]$ (where L is 2,2′-bipyridyl or 1,10-phenanthroline).

RESULTS AND DISCUSSION

The hexaisothiocyanatovanadates(II) (Table 1) were obtained by addition of the appropriate organic chloride or bromide to an aqueous solution containing stoicheiometric amounts of vanadium(II) bromide [6] and ammonium thiocyanate, with careful exclusion of air.

TABLE 1

Analyses (%) and diffuse-reflectance spectra (cm^{-1})

Compound	Analyses [a]				Diffuse-reflectance spectra [b]			
	C	H	N	V				
$[NMe_4]_4[V(NCS)_6]\cdot H_2O$	36.7	7.1	19.9	7.1	R.t. 32 000vs,vbr	25 000m	22 000 (sh)	15 500m
	(37.0)	(7.1)	(19.6)	(7.1)	L.t. 31 500vs,vbr	24 300m	22 500m	15 750m
$[NEt_4]_4[V(NCS)_6]\cdot H_2O$	48.8	8.9	14.5	5.2	R.t. 31 000vs,vbr	24 500m	21 750 (sh)	15 000m
	(48.6)	(8.8)	(14.9)	(5.4)	L.t.	24 250m [c]	22 000 (sh)	15 500m
$[Hhex]_4[V(NCS)_6]\cdot H_2O$	35.5	5.4	31.3	5.3	R.t. 32 500s,vbr	23 500m	21 100 (sh)	15 000m
	(36.7)	(5.5)	(31.4)	(5.2)	L.t. 32 000s,vbr	23 500m	21 100 (sh)	15 100m
$[Hpy]_4[V(NCS)_6]$	42.9	3.3	19.3	7.2	R.t.			15 000 (sh) [c]
	(43.4)	(3.4)	(19.5)	(7.1)	L.t.			15 000 (sh) [c]

[a] Calculated values are given in parentheses. [b] R.t. = Room temperature, L.t. = liquid-nitrogen temperature. [c] Very broad absorption without definite peaks above these frequencies.

The i.r. assignments (Table 2), made by comparisons with the spectra of the cation chlorides, show that the thiocyanato-groups are *N*-bonded.[1] The metal–nitrogen stretching vibrations, ν(MN), are similar to the value (307 cm^{-1}) of the potassium salt,[2] and higher than for hexaisothiocyanates of bivalent metal ions [7] later in the first transition series. The i.r. spectra (200—4 000 cm^{-1}) of $[NEt_4]_4[Ni(NCS)_6]$ and $[NEt_4]_4[V(NCS)_6]$ differ only in that strong ν(M–NCS) absorptions are at 239 cm^{-1} (as found earlier [7]) and 305 cm^{-1} respectively.

The thiocyanates (with the exception of the Hhex salt) have $\mu_{\text{eff.}}$ close to the spin-only value of 3.87 B.M.† and obey the Curie law (Table 2) as expected for compounds with a $^4A_{2g}$ ground term in an octahedral field. Repeat preparations of the Hhex salt gave essentially the same microanalytical figures and high magnetic moment. It is possible that the salt contained a small amount of paramagnetic impurity of low molecular weight.

The three *d–d* transitions expected for octahedral vanadium(II), *i.e.* $^4A_{2g}\rightarrow{}^4T_{2g}$ (ν_1), $^4A_{2g}\rightarrow{}^4T_{1g}(F)$($\nu_2$), and $^4A_{2g}\rightarrow{}^4T_{1g}(P)$ (ν_3), have been found in the spectra of hexahydrated vanadium(II) salts [6] and of tris(ethylenediamine)vanadium(II) complexes.[8] With unsaturated ligands such as substituted imidazoles [4] and pyridines,[5-8] metal-to-ligand charge-transfer bands obscure ν_2 and ν_3. The bands at *ca.* 15 000 cm^{-1} in the spectra (Table 1) are assigned to ν_1. Since the ν_1 band frequency gives 10*Dq*, NCS^- lies below ethylenediamine ($\nu_1 \simeq$ 15 500 cm^{-1}) [8] and above H_2O ($\nu_1 \simeq$ 12 000 cm^{-1}) [3,8] in the spectrochemical series for vanadium(II). This is the usual position for *N*-bonded thiocyanate.[9a] Except for the pyridinium salt which showed strong ill defined absorption above 15 000 cm^{-1}, the spectra contain two bands or shoulders at *ca.* 25 000 and 21 500 cm^{-1} where ν_2 would be expected, and ν_3 is obscured by intense charge-transfer absorption above 30 000 cm^{-1}. Marked splitting of the ν_2 band is not likely for the octahedral anion $[V(NCS)_6]^{4-}$, and in any case ν_1 although broad is unsplit. If the band at 21 500 cm^{-1} is assigned to ν_2, values of *B* of *ca.* 670 cm^{-1} are calculated [6,8] (the free-ion

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† Throughout this note: 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 Oe ≈ 79.58 A m^{-1}.

value is [9b] 766 cm^{-1}), but if ν_2 is taken as 25 000 cm^{-1}, values greater than 766 cm^{-1} are obtained. The assignment of the band at 25 000 cm^{-1} is uncertain. The Tanabe–Sugano diagram shows that the spin-forbidden $^4A_{2g}\rightarrow{}^2T_{2g}$ transition should occur in the same region as ν_2, but the band at 25 000 cm^{-1} has greater intensity than would be expected. These spectra differ somewhat from the reflectance spectrum[2] of $K_4[V(NCS)_6]$, but resemble the spectrum reported for this compound in saturated aqueous K[SCN] except that the band at 25 000 cm^{-1} is not resolved in the solution spectrum.

TABLE 2

Infrared absorptions (cm^{-1}) and magnetic data of thiocyanatovanadates(II) [a]

Compound	ν(CN)	ν(CS)	δ(NCS)	ν(MN)	$\mu_{\text{eff.}}$ [b]/B.M.	θ [c]/°	$10^6\chi_L$ [d]/c.g.s. units
$[NMe_4]_4[V(NCS)_6]\cdot H_2O$	2 075vs,br	786m	488s	312vs,br	3.86	6	458
$[NEt_4]_4[V(NCS)_6]\cdot H_2O$	2 085vs,br	(782vs)	482s	343w 305vs,br	3.84	0	648
$[Hhex]_4[V(NCS)_6]\cdot H_2O$	2 090 (sh) 2 070vs,br	(812m) (780m)	480w	310m 290m	4.25	3	664 (649)
$[Hpy]_4[V(NCS)_6]$	2 065vs,br	790m,br	485m	304vs 348m	3.76	0	363

[a] Wavenumbers in parentheses indicate that counter-ion absorptions render the assignment uncertain. [b] At 295 K, and corrected for temperature-independent paramagnetism by subtraction of 100 × 10^{-6} c.g.s. units from the molar susceptibility values. [c] Curie–Weiss law taken as $\chi_A^{-1} \propto (T + \theta)$. [d] χ_L is the diamagnetic correction calculated entirely from Pascal's constants except for the value in parentheses which was derived from an experimental determination of the diamagnetism of the cation halide.

Although a single-crystal structure of $[NEt_4]_4[Ni(NCS)_6]$ has not been reported, it is believed[7] to contain octahedral anions in which the thiocyanate group is *N*-bonded to the metal ion. *X*-Ray powder photographs show that this complex and $[NEt_4]_4[V(NCS)_6]$ are isomorphous, emphasising the structural analogies between d^3 and d^8 metal ions.

EXPERIMENTAL

As an example the preparation of $[NEt_4]_4[V(NCS)_6]\cdot H_2O$ is described. An aqueous solution of tetraethylammonium bromide (7.4 g, 0.035 mol) was added with shaking to an aqueous solution of vanadium(II) bromide hexahydrate (2.6 g, 0.008 3 mol) and ammonium thiocyanate (4.0 g, 0.053 mol). The green hexaisothiocyanatovanadate(II) salt quickly separated in *ca.* 60% yield. It was filtered off, washed with ice-cold water, and dried in vacuum at room temperature. Attempts to isolate tetrakis(thiocyanato)-vanadates by the use of molar ratios of CNS$^-$: V^{2+} even as low as 1 : 1 gave the hexakis compounds. All operations were carried out under nitrogen or in vacuum because the complexes soon become yellow or orange in air.

Vanadium was determined by ignition to V_2O_5 at 800 °C after treatment of the solid with a few drops of concentrated sulphuric and nitric acids, or by atomic absorption. A Perkin-Elmer P.E. 306 spectrometer was used with an air–acetylene reducing flame and calibrated with standard vanadium solutions supplied by B.D.H. Ltd. The complexes were digested in concentrated sulphuric and nitric acids before appropriate dilution.

Magnetic measurements were carried out down to liquid-nitrogen temperature on a Gouy balance supplied by Newport Instruments Ltd., Newport Pagnell, England. Diffuse-reflectance spectra were recorded on a Unicam SP 700C spectrophotometer with the SP 735 reflectance attachment and a lithium fluoride reference. Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 577 spectrophotometer over the range 200—4 000 cm^{-1}. Polythene plates were used in the 200—600 cm^{-1} region, and KBr plates elsewhere. *X*-Ray powder photographs of samples in sealed Lindemann capillaries were taken with a Philips type P.W. 1026 Debye–Scherrer camera (diameter 114.6 mm) mounted on a Philips *X*-ray generator. Copper K_α radiation was used, with a nickel filter.

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REFERENCES

[1] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Miles, *Co-ordination Chem. Rev.*, 1971, **6**, 407; A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231.

[2] G. Trageser and H. H. Eysel, *Inorg. Chem.*, 1977, **16**, 713.

[3] L. F. Larkworthy, B. J. Tucker, and A. Yavari, Chemical Society Autumn Meeting, University of Reading, England, September 1975, Abstract B.8.

[4] M. Ciampolini and F. Mani, *Inorg. Chim. Acta*, 1977, **24**, 91.

[5] L. F. Larkworthy and B. J. Tucker, *Inorg. Chim. Acta*, 1978, **33**, 167.

[6] L. F. Larkworthy, K. C. Patel, and D. J. Phillips, *J. Chem. Soc.* (*A*), 1970, 1095; H. J. Seifert and T. Auel, *Z. anorg. Chem.*, 1968, **360**, 50.

[7] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 715, 823.

[8] M. M. Khamar, L. F. Larkworthy, K. C. Patel, D. J. Phillips, and G. Beech, *Austral. J. Chem.*, 1974, **27**, 41.

[9] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, (*a*) p. 577, (*b*) p. 1116.