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Synthesis and Characterization of Vanadium(II) Complexes with Poly(1-pyrazolyl)methane Ligands

FABRIZIO MANI

Istituto di Chimica Generale ed Inorganica dell'Università, Laboratorio CNR, Florence, Italy

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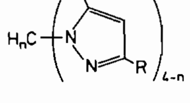
By reaction of the ligands 1,1'-methylenedipyrazole (H_2Cpz_2) and 1,1'-methylenebis(3,5-dimethylpyrazole) (H_2Cdmpz_2) with vanadium(II) salts, six-co-ordinate complexes of the formula $[VL_2X_2]$ *(*$L = H_2Cpz_2$, X = *Cl, Br, I, NCS;* $L = H_2Cdmpz_2$, X = *Br, NCS) are formed. The above reactions in the presence of sodium tetraphenylborate or tetra-n-butylammonium hexafluorophosphate led to polymeric six-co-ordinate* $[V(H_2Cpz_2)_2Cl]BPh_4$*, monomeric five-co-ordinate* $[V(H_2Cdmpz_2)_2Cl]Y$ *(Y =* BPh_4, PF_6*) and monomeric six-co-ordinate* $[V(H_2Cpz_2)_3](BPh_4)_2$ *complexes. Cationic six-coordinate species of the formula* $[V(HCpz_3)_2]Y_2$ *(Y = Br,* PF_6*) and* $[V(HCpz_3)_2]_2[V(NCS)_6]$ *are formed with the potentially tridentate ligand tris(1-pyrazolyl)methane (*$HCpz_3$*). The complexes have been characterized by means of their electronic and magnetic properties.*

Introduction

The chemistry of coordination compounds of vanadium(II) and chromium(II) has been the object of study for a number of years in this laboratory [1, 2].

Among the ligands which form stable complexes with these two ions some poly(1-pyrazolyl)alkanes (I) are found to give a variety of new complexes with vanadium(II) and chromium(II) salts. It is of interest to compare the coordinating behaviour towards these ions of the ligands I with that of the poly(1-pyrazolyl)borates [2] which are anionic ligands isoelectronic with the neutral poly(1-pyrazolyl)alkanes.



(I) n = 2, R = H, H_2Cpz_2
n = 2, R = CH_3, H_2Cdmpz_2
n = 1, R = H, $HCpz_3$

Chromium(II) complexes derived from the ligands I have been reported in another publication [3]. In this paper we report the synthesis and characterization of the compounds obtained by the reaction of some vanadium(II) salts with the ligands 1,1'-methylenedipyrazole (H_2Cpz_2, I, n = 2, R = H), 1,1'-methylenebis(3,5-dimethylpyrazole) (H_2Cdmpz_2, I, n = 2, R = CH_3), and tris(1-pyrazolyl)methane ($HCpz_3$, I, n = 3, R = H).

The complexes obtained with the ligand H_2Cpz_2 have general formulae $[VL_2X_2]$ (X = Cl, Br, I, NCS), $[VL_2Cl]BPh_4$ and $[VL_3](BPh_4)_2$. With the ligand H_2Cdmpz_2 complexes with formula $[VL_2X_2]$ (X = Br, NCS) and $[VL_2Cl]Y$ (Y = BPh_4 PF_6) have been obtained. Finally the complexes with the ligand $HCpz_3$ have formula $[VL_2]Y_2$ (Y = Br, PF_6) and $[VL_2]_2[V(NCS)_6]$. The number of complexes of vanadium(II) so far known is still small [1, 4], due to the relatively poor acceptor ability of this ion and to the high sensitivity of vanadium(II) compounds to oxidation by air and water.

Experimental

The ligands 1,1'-methylene dipyrazole and 1,1'-methylene(3,5-dimethylpyrazole) were prepared as already described in the literature [5]. The ligand tris(1-pyrazolyl)methane was obtained from Columbia Organic Chemical, Co. Anhydrous vanadium(II) halides were synthesized by the method previously reported [6].

All the complexes were prepared under dry nitrogen using absolute ethanol as solvent unless otherwise stated. Starting reactants were usually 2 mmol of vanadium(II) salt dissolved in 30 ml of the appropriate solvent and a saturated solution of the ligand.

$V(H_2Cpz_2)_2X_2$, (X = Cl, Br, I); $V(H_2Cdmpz_2)_2Br_2$

Solutions in n-butanol of the reactants in the stoicheiometric ratio were concentrated by heating until crystals separated from the mixture. Di-n-butyl ether was eventually added to induce crystallization.

TABLE I. Analytical Data for the Complexes.

Complex	Colour	Found (%)			Calcd (%)		
		C	H	N	C	H	N
$[V(H_2Cpz_2)_2Cl_2]$	dark red	40.2	4.05	26.4	40.20	3.85	26.79
$[V(H_2Cpz_2)_2Br_2]$	dark red	32.9	3.46	21.9	33.15	3.19	22.09
$[V(H_2Cpz_2)_2I_2]$	lilac	28.3	2.91	18.5	27.98	2.68	18.55
$[V(H_2Cpz_2)_2(NCS)_2]$	green	40.8	3.50	29.9	41.46	3.48	30.22
$[V(H_2Cpz_2)_3](BPh_4)_2$	green	72.6	5.65	14.8	73.04	5.70	14.84
$[V(H_2Cpz_2)_2Cl]BPh_4$	violet	65.4	5.40	15.5	65.02	5.17	15.46
$[V(H_2Cdmpz_2)_2Br_2]$	grey-violet	42.8	5.50	17.9	42.66	5.20	18.09
$[V(H_2Cdmpz_2)_2(NCS)_2]^a$	green	50.4	5.90	23.7	50.07	5.60	24.33
$[V(H_2Cdmpz_2)_2Cl]BPh_4{}^b$	pink	67.1	6.47	13.9	67.86	6.45	13.76
$[V(H_2Cdmpz_2)_2Cl]PF_6$	pink	41.2	5.47	17.5	41.28	5.04	17.50
$[V(HCpz_3)_2]Br_2$	red-brown	37.9	3.08	26.6	37.57	3.16	26.30
$[V(HCpz_2)_2](PF_6)_2$	light-brown	31.1	2.68	21.8	31.20	2.61	21.85
$[V(HCpz_3)_2]_2[V(NCS)_6]^c$	green-brown	39.4	3.13	30.5	39.03	2.73	30.34

[a] S: calcd. 11.13; found 10.9. [b] Cl: calcd. 4.35; found 4.43. [c] S: Calcd. 14.09; found 14.0

$VL_2(NCS)_2$, ($L = H_2Cpz_2$, H_2Cdmpz_2)

A solution of sodium thiocyanate was added to a solution of vanadium(II) chloride. The mixture was filtered to eliminate sodium chloride and added to a warm solution of the appropriate ligand in the stoicheiometric ratio. Crystalline products readily formed upon heating the resulting solutions.

$V(H_2Cpz_2)_3(BPh_4)_2$

This compound immediately formed upon adding a solution of sodium tetraphenylborate to a solution of vanadium(II) chloride containing the ligand in excess to the stoicheiometric ratio.

VL_2ClY, ($L = H_2Cpz_2$, $Y = BPh_4$; $L = H_2Cdmpz_2$, $Y = BPh_4, PF_6$)

To a boiling solution of vanadium(II) chloride and the appropriate ligand in the stoicheiometric ratio, a boiling solution of sodium tetraphenylborate or tetra-n-butylammonium hexafluorophosphate was added. Crystalline products have been obtained after the resulting solutions were boiled for a short time. All efforts to obtain analogous compounds starting from vanadium(II) bromide failed. If sodium tetrafluoroborate is used in the above reactions, yellow crystalline products are obtained with a B:V:F ratio 1:2:10. In these compounds, which still contain vanadium(II), the decomposition of tetrafluoroborate anion led, probably, to fluoride adducts whose characterization has not been possible.

$V(HCpz_3)_2Br_2$

This compound has been readily obtained upon adding a solution of vanadium(II) bromide to a solution of the ligand in the stoicheiometric amount.

$V(HCpz_3)_2(PF_6)_2$

This compound immediately formed upon adding a boiling solution of tetra-n-butylammonium hexafluorophosphate to a boiling solution of vanadium(II) chloride and the ligand.

$V_3(HCpz_3)_4(NCS)_6$

A warm solution of vanadium(II) thiocyanate was added to a boiling solution of the ligand. After the resulting solution has been concentrated by heating, crystals separated from the mixture.

In all these preparations the solid products formed from the solutions were washed by decantation with a mixture of absolute ethanol and diethyl ether, filtered, washed with diethyl ether alone, and finally dried off by standing in a stream of dry nitrogen at 100 °C. The tetraphenylborate derivatives were washed also with water to eliminate crystallized sodium chloride.

The analytical data are reported in Table I.

Magnetic and spectrophotometric measurements have been performed with the apparatus already described [7] on samples contained in suitable air-tight containers (Gouy tube and UV cells) filled in dry-box under inert atmosphere.

Results and Discussion

Complexes with the Ligands H_2Cpz_2 and H_2Cdmpz_2

The potentially bidentate ligands H_2Cpz_2 and H_2Cdmpz_2 react with vanadium(II) salts giving complexes of different stoicheiometry depending on the coordination power of the anions in solution. Halides and pseudohalides of vanadium(II) form complexes

TABLE II. Physical Data for the Complexes.

Complex	μ_{eff}/B.M. (295 K)	μ_{eff}/B.M. (84 K)	Electronic Spectra (10^{-3} $\tilde{\nu}$/cm^{-1})
$[V(H_2Cpz_2)_2Cl_2]$	3.78		13.9; 19.0
$[V(H_2Cpz_2)_2Br_2]$	3.83		11.2 sh; 14.0; 19.3; 26.6
$[V(H_2Cpz_2)_2I_2]$	3.80		10.8 sh; 13.4; 19.1
$[V(H_2Cpz_2)_2(NCS)_2]$	3.81		16.0; 22.5 sh; 26.0
$[V(H_2Cpz_2)_3](BPh_4)_2$	3.83		16.4; 22.2 sh; 26.7
$[V(H_2Cpz_2)_2Cl]BPh_4$	3.11	1.80	15.2 sh; 19.6; 26.5
$[V(H_2Cdmpz_2)_2Br_2]$	3.80		10.3; 14.3 sh; 18.7
$[V(H_2Cdmpz_2)_2(NCS)_2]$	3.79		16.0; 22.6 sh; 26.8
$[V(H_2Cdmpz_2)_2Cl]BPh_4$	3.82	3.80	12.5; 19.2
$[V(H_2Cdmpz_2)_2Cl]PF_6$	3.83	3.82	13.4; 19.0
$[V(HCpz_3)_2]Br_2$	3.83		19.0 sh; 23.8
$[V(HCpz_3)_2](PF_6)_2$	3.81		19.1 sh; 24.1
$[V(HCpz_3)_2]_2[V(NCS)_6]$	3.80^a	3.81	18.2 sh

^{a}Average value per metal atom.

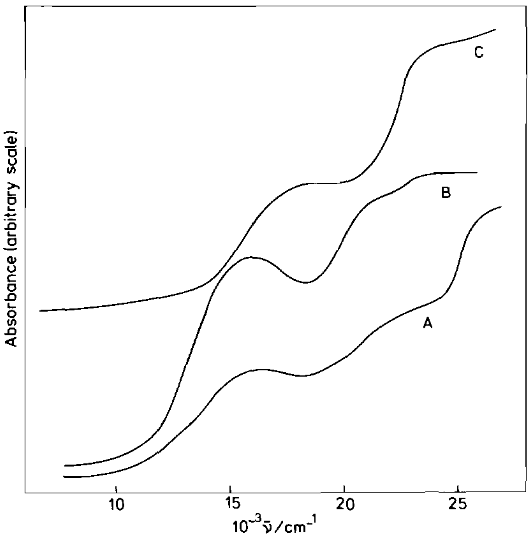


Fig. 1. Reflectance spectra of: A, $[V(H_2Cpz_2)_3](BPh_4)_2$; B, $[V(H_2Cpz_2)_2(NCS)_2]$; C, $[V(HCpz_3)_2](BPh_4)_2$.

with a metal-to-ligand ratio 1:2 and stoicheiometry VL_2X_2 (L = H_2Cpz_2, X = Cl, Br, I, NCS; L = H_2Cdmpz_2, X = Br, NCS). The reaction of the same ligands in the presence of anions with poorly coordinating ability, namely BPh_4^- and PF_6^-, led to compounds of stoicheiometry VL_2XY (L = H_2Cpz_2, X = Cl, Y = BPh_4; L = H_2Cdmpz_2, X = Cl, Y = BPh_4, PF_6) and $V(H_2Cpz_2)_3(BPh_4)_2$.

The complexes with general formula $[VL_2X_2]$ (L = H_2Cpz_2, H_2Cdmpz_2) and $[V(H_2Cpz_2)_3](BPh_4)_2$ have magnetic moment values at room temperature in the range 3.78–3.83 B.M. close to the spin-only value of 3.87 B.M. for a d^3 configuration (Table II).

The ligand-field spectrum of the complex $[V(H_2Cpz_2)_3](BPh_4)_2$ in the solid state (Table II and Fig. 1) exhibits a band at 16400 cm^{-1} and a poorly resolved shoulder at *ca.* 22000 cm^{-1}. This spectrum is quite similar to the reflectance spectrum of $K[V(H_2Bpz_2)_3]\cdot C_2H_5OH$ which is known to possess a slightly distorted octahedral geometry [2]. On this basis an octahedral coordination geometry can be safely assigned to the present 1:3 complex too. The bands at 16400 and *ca.* 22000 cm^{-1} can be assigned to the first two spin-allowed d–d transitions, namely $^4A_{2g} \rightarrow {}^4T_{2g}$, ν_1, and $^4A_{2g} \rightarrow {}^4T_{1g}$, ν_2, which are predicted for the octahedral d^3 configuration. The third transition, $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, is calculated to occur at *ca.* 34000 cm^{-1} by using the frequencies of the ν_1 and ν_2 transitions and well known methods [8]. Consequently the ν_3 transition is outside the spectral range investigated. The band at *ca.* 26700 cm^{-1} is thus attributable to a metal-to ligand charge-transfer transition.

In the reflectance spectra of the $[VL_2X_2]$ derivatives (L = H_2Cpz_2, X = Cl, Br, I; L = H_2Cdmpz, X = Br) three bands or shoulders are detectable between 11000 and 19000 cm^{-1} (Table II and Fig. 2). These spectral features are significantly different from those of the above 1:3 complexes and are typical of a more or less distorted *trans*-octahedral d^3 configuration [1, 4].

The spectra of the two thiocyanate complexes $[VL_2(NCS)_2]$ (L = H_2Cpz_2, H_2Cdmpz_2) (Table II and Fig. 1) are quite similar in shape and in frequency of the absorption maxima to that of the [V(H_2-

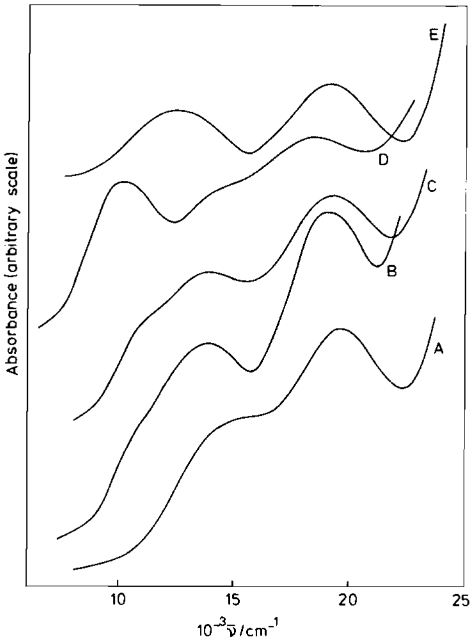


Fig. 2. Reflectance spectra of: A, $[V(H_2Cpz_2)_2Cl]BPh_4$; B, $[V(H_2Cpz_2)_2Cl_2]$; C, $[V(H_2Cpz_2)_2Br_2]$; D, $[V(H_2Cdmpz_2)_2Br_2]$; E, $[V(H_2Cdmpz_2)_2Cl]BPh_4$.

$Cpz_2)_3](BPh_4)_2$ derivative and are indicative of a slightly distorted octahedral geometry. The spectral behaviour of the two thiocyanate complexes are probably due to the greater ligand-field strength of the thiocyanate ion (N-bonded) which does not differ from that of pyrazolide as much as that of the halides.

The complexes with formula $[VL_2Cl]Y$ ($L = H_2Cpz_2$, $Y = BPh_4$; $L = H_2Cdmpz_2$, $Y = BPh_4$, PF_6) have physical properties which depend on the nature of the ligands, in spite of the formal analogy in the stoicheiometry.

The magnetic moment value of $[V(H_2Cpz_2)_2Cl]BPh_4$ at room temperature is well below the spin-only value of 3.87 B.M. for three unpaired electrons and varies from 3.11 to 1.80 B.M. within the range 290–84 K (Table II). The electronic spectrum of the complex (Table II and Fig. 2) is substantially similar to that of the six-co-ordinate $[V(H_2Cpz_2)_2Cl_2]$. Magnetic and spectrophotometric properties together suggest a polymeric structure for the $[V(H_2Cpz_2)_2Cl]BPh_4$ complex with six-co-ordinate vanadium(II) ions linked by bridging chlorine atoms presumably *trans* to one another.

The room temperature magnetic moment values, 3.82–3.83 B.M., of the two complexes $[V(H_2Cdmpz_2)_2Cl]Y$ ($Y = BPh_4$, PF_6) are virtually independent of temperature in the range 290–84 K (Table II). This magnetic behaviour rules out a halide-bridged structure which would lead to a magnetic interaction between vanadium(II) atoms as found in $[V(H_2Cpz_2)_2Cl]BPh_4$. Therefore the stoicheiometry by itself suggests that the complexes $[V(H_2Cdmpz_2)_2Cl]BPh_4$ and $[V(H_2Cdmpz_2)_2Cl]PF_6$ may contain five-co-ordinate vanadium(II). Reflectance spectra of the two complexes with two broad bands at *ca.* 13000 and 19000 cm^{-1} (Table II and Fig. 2) cannot be assigned on the basis of qualitative energy-level schemes for a nearly regular trigonal-bipyramidal or square-pyramidal d^3 configuration [9, 10] presumably due to a large distortion of the co-ordination polyhedron from the two limiting geometries. As a matter of fact several nickel(II) complexes (high-spin d^8 configuration) with chelating ligands, having distorted trigonal-bipyramidal structures [11], have electronic spectra similar in shape and comparable in the frequency of absorption maxima to those of the two vanadium(II) complexes here reported.

The five-co-ordination of the two $[V(H_2Cdmpz_2)_2Cl]Y$ complexes appears to be unique among the vanadium(II) complexes so far known, all of which are six-co-ordinate. In this context it is interesting to note that the anionic ligand dihydrobis(3,5-dimethylpyrazolyl)borate, $H_2Bdmpz_2^-$, which is isoelectronic with the neutral H_2Cdmpz_2 ligand forms a square-planar chromium(II) complex, CrL_2, but no complex with vanadium(II) [12]. The less sterically hindered ligand dihydrobis(1-pyrazolyl)borate, $H_2Bpz_2^-$, on the other hand, forms a square-planar chromium(II) complex, CrL_2, and a six-co-ordinate vanadium(II) complex with the formula $K[V(H_2Bpz_2)_3]\cdot C_2H_5OH$ [2]. On the other hand, quite similar results are obtained with both vanadium(II) and chromium(III) [3] and the ligands H_2Cpz_2 and H_2Cdmpz_2: polymeric six-co-ordinate $[M(H_2Cpz_2)_2X]^+$ (M = V, Cr) and monomeric five-co-ordinate $[M(H_2Cdmpz_2)_2X]^+$ (M = V, Cr) species have been isolated.

Most of the complexes reported here are soluble in solvents such as acetonitrile and N,N′-dimethylformamide. A more or less pronounced decomposition or oxidation of the complexes, however, takes place in these solvents as the absorption spectra appear markedly different from the solid reflectance spectra.

Complexes with the Ligand $HCpz_3$

This potentially tridentate ligand reacts with solutions of VBr_2 or $V(PF_6)_2$ giving complexes of general formula $[VL_2]Y_2$ ($Y = Br, PF_6$). Using a solution of $V(NCS)_2$ a complex with the formula $[VL_2]_2[V(NCS)_6]$ has been obtained.

The $[VL_2]Y_2$ complexes have magnetic moments, 3.83–3.82 B.M., normal for a d^3 configuration. Their electronic spectra are quite similar to each other and closely resemble that of the octahedral $[V(HBpz_3)_2]$ [2] ($HBpz_3$ = hydrotris(1-pyrazolyl)borate). The two d–d bands at *ca.* 19000 and 24000 cm^{-1} in the spectra of the $[V(HCpz_3)_2]Y_2$ complexes (Table II and Fig. 1) are thus assigned to the first two transitions expected for the octahedral d^3 configuration.

The $[V(HCpz_3)_2]_2[V(NCS)_6]$ derivative has a magnetic moment value (per metal atom) of *ca.* 3.80 B.M. which does not vary with temperature (Table II). The reflectance spectrum of the complex is dominated by an intense charge-transfer band starting from 19000 cm^{-1} with an ill-defined band at *ca.* 18000 cm^{-1}. The latter band can be assigned to the superimposed absorptions of the two octahedral species, $[V(NCS)_6]^{4-}$ and $[V(HCpz_3)_2]^{2+}$, whose ligands have comparable donor strength as also found in the $[VL_2(NCS)_2]$ complexes (L = H_2Cpz_2, H_2-Cdmpz$_2$).

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