Inorganica Chimica Acta, *97* (1985) L31–L33

Synthesis and Characterization of [$V(NCCH_3)_6ZnCl_4$], a Low Valence Vanadium Complex

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Received September 11, 1984

Reaction of vanadium halides with metal alkyls is a frequently used and not always successful route to lower valence vanadium compounds [1], the other methods commonly employed being electrochemical reduction [2, 3] and the use of reducing agents such as zinc dust [4]. Characterization of such low valence vanadium compounds can give much insight into the bonding characteristics of vanadium in its lower oxidation states; this is at present limited primarily due to the experimental difficulties encountered in working with the lower oxidation states of V [5, 6]. Another significant application of such reactions is in the production of highly specific catalytic systems [7], the most well known of which are of course the Ziegler-Natta catalysts [8, 9]. In the homogeneous variety of these catalysts, the active intermediate is thought to be a low-valence transition metal to which an alkyl group is coordinated; however, attempts at isolation and characterization of the active intermediate have proved elusive [10]. With this aim in mind, we investigated the reduction of VCl_3 by $ZnEt_2$ in acetonitrile and tetrahydrofuran (THF); in the strongly coordinating CH_3CN, this yielded the product [$V(NCCH_3)_6ZnCl_4$], whose crystal structure is presented here. The results of complementary investigations of the reaction of VCl_3 with $AlEt_3$ in various solvents have been reported in an earlier communication from this laboratory [11].

Experimental

Syntheses

All experiments were carried out under a dry N_2 or argon atmosphere using standard Schlenkware, drybox and vacuum-line techniques. $ZnEt_2$ was prepared from EtI–EtBr and a Zn–Cu couple as described elsewhere [12]. Elemental analyses were performed by Galbraith Laboratories (Knoxville, Tennessee). IR measurements of solid samples, prepared as nujol mulls between AgCl windows, were carried out on a Perkin-Elmer IR 599 (double beam) spectrometer. UV–Vis measurements of solutions under argon atmosphere were carried out on a Pye-Unicam SP8-100 (d. beam) spectrometer.

[$V(NCCH_3)_6ZnCl_4$]

5 ml of 0.1 M $ZnEt_2/CH_3CN$ and 5 ml of 0.1 M VCl_3/CH_3CN were cooled to *ca.* –85 °C and the VCl_3 solution added slowly to the $ZnEt_2$ (via syringe and septa) with stirring. An intense violet coloration [11] was obtained immediately on mixing the reactants. After keeping the solution, without reduction in volume, for 5–6 h at –20 °C, greenish-black crystals, insoluble in CH_3CN were obtained. These were washed with the solvent, dried and sealed under vacuum. Variation of the V/Zn ratio did not yield a different product. UV-Vis., react. mixt. in CH_3CN (nm): 487 (ϵ: 600, CT); 680 (ϵ: 70, $^4A_{2g} \rightarrow {}^4T_{1g}$, V(II)). IR ($cm^{-1}$): 2920–2830 ($\nu$(CH), s., br.); 2280 ($\nu$(C≡N), s.); 2310 ($\nu$(C≡N), s.); 1450 ($\nu_{as}(CH_3)$, s., br.); 1370 ($\nu_s(CH_3)$, s., br.); 715 (s.); 415 (C–C≡N bend, v.s.).

[$V(THF)_4ZnCl_4$]

5 ml 0.1 M $ZnEt_2$/THF and 5 ml 0.1 M VCl_3/THF were cooled to *ca.* –40 °C. The VCl_3 solution was slowly added to the $ZnEt_2$ (via syringe and septa) with constant stirring. An intense violet coloration was immediately obtained. On slight reduction of the volume of the reaction mixture and keeping for 3 days at –20 °C, purple-black crystals, insoluble in THF, were obtained. Washed with THF, dried and sealed *in v acuo*. UV-Vis., reac. mixt. in THF, (nm): 483 (ϵ: 390, CT); 600 (ϵ: 72). IR (cm^{-1}): 1455; 1372 ($\nu(CH_3)$, v.s.); 1035 (ν(C–O–C), m.s.); 1015 (s.); 362 ($\nu(V\text{–}O_{THF})$, s.)

Crystal Structure of [$V(NCCH_3)_6ZnCl_4$]

Determination: A suitable crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was mounted in a capillary and sealed under vacuum. A Picker 4-circle diffractometer interfaced to a PDP 8/a minicomputer and employing the peak search, centering, indexing and data collection package of the National Research Council of Canada [13] was used. Mo K_α radiation (λ = 0.71069 Å) with a graphite monochromator was employed. The θ–2θ scan mode was used. The structure was solved by conventional heavy-atom techniques, the Zn and V atoms being located by Patterson synthesis. Block-diagonal least-squares refinement yielded the positions of all remaining non-H atoms. With anisotropic thermal parameters

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(U_{ij}'s) a final R-factor of 0.069 (0.086 weighted) was obtained.

Crystal Data: $ZnVCl_4N_6C_{12}H_{18}$, FW = 504.49; Space group $P\bar{1}$; a = 11.832(5) Å, b = 12.592(5) Å, c = 11.801(5) Å; α = 62.17(1)°, β = 119.90(1)°, γ = 117.78(1)°; V = 1283.92 Å^3; D_{obs} = 1.29 g cm^{-3}, D_{calc} = 1.304 g cm^{-3}; Z = 2; Unique reflections ($I > 3\sigma(I)$), 2018, pamts., 1.64; R = 0.097, R_w = 0.048 (Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/(\sigma(F_o))^2$, $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = ((w(|F_o| - |F_c|))^2/(\Sigma w|F_o|)^2)^{1/2}$). GOF (= $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, N_o and N_v, respectively, N^{o} of observations and variables) = 4.27.

Table I lists the final positional parameters, with e.s.d.s, for $[V(NCCH_3)_6ZnCl_4]$. The labeling scheme is illustrated in the ORTEP drawing depicted in Fig. 1. Table II lists the important bonded contacts, with estimated standard deviations.

Results and Discussion

$[V(NCCH_3)_6ZnCl_4]$, depicted in Fig. 1, consists of a hexakis(acetonitrile) V(II) species, octahedrally coordinated and with a formal charge of +2, and a tetrachlorozincate moiety, with a formal charge of −2, in which the Zn has (near) tetrahedral coordina-

TABLE I. Positional Parameters, with e.s.d.s for $[V(NCCH_3)_6ZnCl_4]$.

Atom	x	y	z
Zn	0.2658(1)	0.2878(1)	0.7340(2)
V	0.9108(2)	0.2826(2)	0.0893(2)
Cl1	0.2418(4)	0.2346(4)	0.5712(4)
Cl2	0.0644(3)	0.2351(4)	0.7583(4)
Cl3	0.4294(3)	0.2358(3)	0.9360(4)
Cl4	0.3373(4)	0.5127(3)	0.6624(4)
N1	0.7329(9)	0.1144(9)	0.1367(9)
N2	0.8602(9)	0.115(1)	−0.018(1)
N3	0.9562(9)	0.3428(8)	0.2054(9)
N4	1.0942(8)	0.3434(9)	0.0446(9)
N5	1.0188(9)	0.1132(9)	0.2663(9)
N6	0.7953(8)	0.3427(8)	−0.0937(9)
C1a	0.640(1)	0.040(1)	0.164(1)
C1b	0.516(1)	−0.054(1)	0.198(1)
C2a	0.837(1)	0.039(1)	−0.063(1)
C2b	0.803(1)	−0.054(1)	−0.126(1)
C3a	0.976(1)	0.390(1)	0.277(1)
C3b	0.999(2)	0.459(1)	0.365(2)
C4a	1.193(1)	0.391(1)	0.026(1)
C4b	1.326(1)	0.456(2)	0.004(2)
C5a	1.066(1)	0.038(1)	0.363(1)
C5b	1.126(1)	−0.054(1)	0.485(1)
C6a	0.724(1)	0.391(1)	−0.192(1)
C6b	0.637(1)	0.457(1)	−0.322(1)

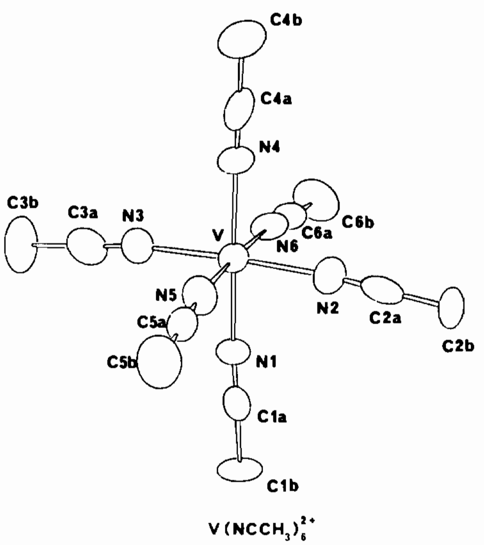

Fig. 1a. ORTEP drawing of the $[V(NCCH_3)_6]^{II}$ moiety, showing labeling scheme.

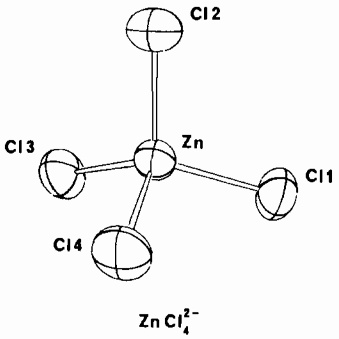

Fig. 1b. ORTEP drawing of the tetrachlorozincate moiety, showing labeling scheme.

TABLE II. Relevant Bond Lengths and Angles, with e.s.d.s for $[V(NCCH_3)_6ZnCl_4]$.

Distances (e.s.d), Å

Zn−Cl1	2.253(5)	N2−C2a	1.17(2)
Zn−Cl2	2.258(4)	N3−C3a	1.13(2)
Zn−Cl3	2.260(5)	N4−C4a	1.12(2)
Zn−Cl4	2.280(5)	N5−C5a	1.16(2)
V−N1	2.11(1)	N6−C6a	1.13(2)
V−N2	2.08(1)	C1a−C1b	1.50(2)
V−N3	2.11(1)	C2a−C2b	1.47(2)
V−N4	2.14(1)	C3a−C3b	1.50(2)
V−N5	2.11(1)	C4a−C4b	1.49(2)
V−N6	2.12(1)	C5a−C5b	1.46(2)
N1−C1a	1.14(2)	C6a−C6b	1.46(2)

Angles (e.s.d), deg

Cl1−Zn−Cl2	116.6(2)	N2−V−N6	88.6(4)
Cl1−Zn−Cl3	111.8(2)	N5−V−N6	176.3(4)
Cl1−Zn−Cl4	107.2(2)	N3−V−N4	92.1(4)

TABLE II. *(continued)*

Cl2–Zn–Cl3	111.8(2)	N3–V–N6	93.0(4)
Cl2–Zn–Cl4	107.3(2)	N3–V–N5	90.4(4)
Cl3–Zn–Cl4	106.9(2)	N4–V–N5	89.1(4)
N1–V–N2	87.1(4)	N4–V–N6	92.2(4)
N1–V–N3	90.0(4)	V–N1–C1a	173(1)
N1–V–N4	176.8(4)	V–N2–C2a	172(1)
N1–V–N5	88.5(4)	V–N3–C3a	173(1)
N1–V–N6	90.0(4)	V–N4–C4a	174(1)
N2–V–N3	176.7(5)	V–N5–C5a	173(1)
N2–V–N4	90.7(4)	V–N6–C6a	174(1)
N2–V–N5	88.0(5)		

tion. The bond angles (Table II) show that there is some slight deviation from tetrahedral and octahedral coordination, respectively, for the Zn and V atoms; this may be ascribed to crystal packing forces, as the cell packing arrangement has shown the existence of a large void. The average Zn–Cl bond distance, 2.26 Å, agrees well with the 2.26 Å observed in Na_2ZnCl_4 [14], where, however, near perfect tetrahedral cordination for the Zn atoms was observed. The Zn–Cl bond is slightly longer than that observed in 4(ac-py)$_2$ZnCl$_2$ (2.206 Å) [15], $ZnCl_2$ (2.204 Å) and in 4-(CN-py)$_2$ZnCl$_2$ (2.207 Å) [16]. In the $(V(NCCH_3)_6)^{II}$ moiety, substantial $d_\pi \rightarrow \pi^*$ (ligand) interaction would be expected to strenghthen the bond; thus the average V–N distance (2.11 Å) may be compared with that in $[V^{(V)}O(NO_3)_3NCCH_3]$ (2.24 Å) [17] and in $[V^{(II)}(py)_4Cl_2]$ (2.189 Å) [18], the M–L (V–N) interaction in the latter being not as strong as for a cyano ligand. It is also interesting to note that in the title compound, $[V(NCCH_3)_6ZnCl_4]$, only 15 electrons are assignable to the V.

The V–N–C bond angle (173.4° av.) shows a deviation from the expected linearity which has been observed earlier for coordinated CH_3CN [4, 17]; in line with this, the C–C≡N bending frequency in the IR spectrum shifts from 373 cm^{-1} in the free ligand to 415 cm^{-1} in the complex, while the C≡N stretch frequencies are shifted from 2290 and 2245 cm^{-1} (free ligand) to 2310 and 2280 cm^{-1}, also indicating a shortening of the bond in the complex; the latter values may be compared with 2310 and 2285 cm^{-1} observed in $[V^{(II)}(NCCH_3)_4Cl_2]$, [4].

A plausible scheme for the reactions leading to the formation of the product, $[V(NCCH_3)_6ZnCl_4]$, is the possible alkylation of only one coordinative position of the V(III) (through metathetical exchange between $[V(NCCH_3)_3Cl_3]$ and $ZnEt_2$ in CH_3CN) with subsequent displacement of this single ethyl group by the strongly coordinating solvent (CH_3CN), leading to the reduction of V(III) to V(II) (and gaseous hydrocarbon products). This role of the solvent may explain why no V-ethyl bonds are isolated in our product, whereas they are, for instance, when a weakly coordinating solvent such as n-pentane is used, as in the formation of $[VD_2H_5Cl_2]$ from VCl_4 and $ZnEt_2$ in n-pentane [19]. Thus the choice of solvents of low coordinative ability in, for instance, Ziegler-Natta catalysis reactions, is supported, since any transition metal–alkyl bonds existing in the catalytically active intermediate would appear to be stabilized.

Acknowledgement

Partial support of this research through a grant from the National Science Foundation (NSF No. 150-2705A) (U.S.A.) is gratefully acknowledged.

References

1 N. Kano, T. Tanaka and A. Murakami, (Mitsubishi Chem. Ind. Co., Ltd.), *Jpn. Kokai,* No 77 156 195.

2 J. J. Habeeb, L. Neilson and D. G. Tuck, *Can. J. Chem., 55,* 2631 (1977).

3 H.-J. Seifert and B. Gerstenberg, *Z. Anorg. Allg. Chem., 315,* 56 (1962).

4 H.-J. Seifert and T. Auel, *J. Inorg. Nucl. Chem., 30,* 2081 (1968).

5 R. Matsuzaki and Y. Saeki, *Bull. Chem. Soc. Jpn., 53,* 2843 (1980).

6 W. P. Schaefer, *Inorg. Chem., 4,* 642 (1965).

7 G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl., 6,* 790 (1967).

8 K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem., 67,* 541 (1955).

9 G. Natta, *Angew. Chem., 68,* 393 (1956).

10 R. Schrock, S. McLain and J. Sancho, *Pure Appl. Chem., 52,* 729 (1980).

11 P. Chandrasekhar and P. H. Bird, *Inorg. Chem.,* in press.

12 G. E. Coates and K. Wade, (eds.), 'Organometallic Compounds, Vol. I. The Main Group Elements', Methuen, London, 1967.

13 E. J. Gabe, A. C. Larsen, Y. Wang and F. L. Lee, Chem. Divn. of National Research Council of Canada, Ottawa.

14 C. J. J. van Loon and D. Visser, *Acta Crystallogr., Sect. B:, 33,* 188 (1977).

15 W. L. Steffer and G. J. Palenic, *Acta Crystallogr., Sect. B:, 32,* 298 (1976).

16 M. A. Porai-Koshitz, *Ah. Strukt. Khim., 17,* 1124 (1976).

17 F. W. B. Einstein, E. Enwall, D. M. Morris and D. Sutton, *Inorg. Chem., 10,* 678 (1971).

18 E. Brauer and C. Kruger, *Cryst. Struct. Commun., 3,* 421 (1973).

19 K. Jacobs, S. Wagner, W. Schumann and K.-H. Thiele, *Z. Anorg. Allg. Chem., 427,* 75 (1976).