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Structure of Tetrakis(1-vinylimidazole)cobalt(II) Dichloride, $[Co(C_5H_6N_2)_4]Cl_2$

By P. de Vaal, F. B. Hulsbergen and R. A. G. de Graaff

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, PO Box 9502, 2300*RA Leiden, The Netherlands*

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Abstract. $M_r = 506\cdot30$, monoclinic, $P2_1/n$, $a = 11\cdot104\,(2)$, $b = 15\cdot148\,(2)$, $c = 7\cdot306\,(1)$ Å, $\beta = 107\cdot34\,(1)^\circ$, $V = 1173\cdot2\,(5)$ Å^3, $Z = 2$, $D_x = 1\cdot43$, $D_m = 1\cdot46\,(3)$ g cm^{-3}, $F(000) = 523$, $\lambda(\text{Mo }K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo }K\alpha) = 9\cdot32$ cm^{-1}, room temperature, final $R = 0\cdot034$ for 1370 significant reflections $[I > 2\sigma(I)]$. Co^{2+} lies in a tetragonally distorted octahedron of four coordinating N atoms and two *trans* coordinated Cl^- ions. The complex cation formed by the coordination of four 1-vinylimidazole molecules to the Co^{2+} ion has point symmetry $\bar{1}$.

Introduction. Tetragonally distorted octahedral coordination compounds of formula $[M(\text{ligand})_4](\text{anion})_2$ with the anions in a *trans* geometry are of great interest from a ligand-field spectroscopic point of view (McCarthy & Reedijk, 1980).

When pyridine is the ligand and the anions are Cl^- or Br^- several compounds have been studied both spectroscopically and by X-ray diffraction (Long & Clarke, 1978).

With pyrazoles as the ligands the tetragonal distortion is much larger, a phenomenon attributed to hydrogen bonding between the anion and the acidic pyrazole N—H (Reedijk, Stork-Blaisse & Verschoor, 1971; Reimann, Mighell & Mauer, 1967; Reimann, Santoro & Mighell, 1970).

With imidazoles and ligands intramolecular hydrogen bonding is not possible and less tetragonal species are usually found. In the case of $[Co(1\text{-vinylimidazole})_4][SiF_6]$ (Driessen, Hulsbergen, Vermin & Reedijk, 1982), however, a very strong tetragonal distortion occurs (*i.e.* short Co—N distances). It was not clear whether the counter ion or the particular imidazole ligand is responsible for this effect. Therefore, another tetragonal Co compound containing 1-vinylimidazole (henceforth viz) has been studied by X-ray crystal structure analysis; the results are described below.

Experimental. D_m by flotation in *n*-butanol–dibromoethane; violet needles grown from ethanol; $0\cdot35 \times 0\cdot20 \times 0\cdot17$ mm; Enraf–Nonius CAD-4 four-circle diffractometer; graphite-monochromated Mo $K\alpha$; cell constants from setting angles of 24 reflections; Lorentz and polarization corrections; no absorption correction performed as intensity variation in azimuth reflections *ca* 2%; $\theta_{\max} = 25^\circ$; h 0 to 13, k 0 to 18, l −8 to +8; 2179 measured reflections; 2067 independent reflections; $R_{\text{int}} = 0\cdot013$; three standard reflections measured with intensity variation of 9·9% (nonrandom, 87 measurements); intensities corrected for this loss of scattering; 697 unobserved reflections $[I < 2\sigma(I)]$; structure solved by Patterson and Fourier methods; H atoms found from difference Fourier; F values used for least-squares refinement of coordinates and anisotropic temperature factors of non-hydrogen atoms; H atoms refined isotropically; max. and min. electron densities in final $\Delta\rho$ map 0·76 and −0·75 e Å^{-3} (noise level 0·14 e Å^{-3}); ratio of max. LS shift to error 0·03, $w = 1/\sigma^2(F)$, $S = 1\cdot7288$, $R_w = 0\cdot045$; scattering factors and anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974); Leiden University Computer (Amdahl V7B) with programs written or modified by Mrs E. Rutten-Keulemans and R. A. G. de Graaff.

Discussion. Positional parameters and equivalent isotropic B values for the nonhydrogen atoms are listed in Table 1.* The corresponding labelling of the atoms is shown in Fig. 1. The molecular structure of $[Co(viz)_4]Cl_2$ is shown in Fig. 2. The special position $\bar{1}$ is occupied by the Co^{2+} ion at (0,0,0). Each vinylimidazole molecule coordinates through the pyridine-type N atom, forming a nearly regular square around Co. The N(1)*A*—Co—N(1)*B* angles deviate only slightly from 90°. Relevant bond distances and angles are given in Table 2. The metal—nitrogen distances are comparable to those found in $[Co(\text{pyridine})_4]Cl_2$ and $[Ni(\text{pyridine})_4]Cl_2$ (2·18 and 2·13 Å respectively) (Long & Clarke, 1978), but somewhat longer than in the more tetragonally distorted $[Ni(\text{pyrazole})_4Cl_2]$ (2·09 and 2·10 Å) (Reimann *et al.*, 1967) and $[Co(viz)_4][SiF_6]$ (2·10 Å) (Driessen *et al.*, 1982). With respect to the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38770 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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latter we can now conclude that the high tetragonal distortion found is a counter ion effect and not a ligand effect. The Co–Cl distance is exactly the same as the Ni–Cl distance in [Ni(pyrazole)$_4$]Cl$_2$. All intermolecular contacts appear to be normal van der Waals contacts, the shortest being 2·75 (5) Å for H(3)*B*···Cl.

The imidazole rings are almost planar, the largest deviation being 0·003 (2) Å. The N(4)–C(6) bond length indicates some double-bond character, as is the case in other 1-vinylimidazole compounds. The vinyl group is some degrees out of plane, group *A* 4 (1)°, group *B* 16 (1)°, which is comparable to, for example, [Co(viz)$_4$][SiF$_6$] with the vinyl 8° out of plane.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors, with e.s.d.'s in parentheses*

$B_{eq} = \frac{8}{3}\pi^2 \text{ trace } \tilde{\mathbf{U}}$.

	x	*y*	*z*	B_{eq} (Å^2)
Co	0	0	0	3·17 (2)
N(1)*A*	−1717 (3)	395 (2)	489 (4)	3·51 (8)
C(2)*A*	−2878 (4)	506 (3)	−815 (6)	4·89 (13)
C(3)*A*	−3724 (4)	737 (3)	67 (7)	5·33 (14)
N(4)*A*	−3095 (3)	785 (2)	1965 (4)	4·18 (9)
C(5)*A*	−1892 (4)	572 (2)	2128 (6)	3·88 (11)
C(6)*A*	−3536 (5)	1018 (3)	3532 (8)	6·0 (2)
C(7)*A*	−4676 (6)	1177 (5)	3417 (12)	8·6 (3)
N(1)*B*	1068 (3)	1024 (2)	1839 (4)	3·58 (8)
C(2)*B*	1679 (4)	1724 (3)	1310 (6)	4·41 (12)
C(3)*B*	2391 (4)	2140 (3)	2926 (8)	7·4 (2)
N(4)*B*	2207 (3)	1707 (2)	4434 (5)	3·11 (9)
C(5)*B*	1419 (4)	1057 (3)	3702 (5)	4·29 (12)
C(6)*B*	2742 (5)	1869 (3)	6435 (8)	6·4 (2)
C(7)*B*	3680 (7)	2357 (4)	7176 (12)	7·6 (2)
Cl	419 (1)	−1020 (1)	2824 (1)	4·02 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *for* [Co(viz)$_4$]Cl$_2$

Co–Cl 2·508 (1) N(1)*A*–Co–N(1)*B* 92·7 (1)

	A	*B*
Co–N(1)	2·127 (3)	2·166 (4)
N(1)–C(2)	1·366 (5)	1·374 (5)
N(1)–C(5)	1·297 (5)	1·301 (5)
C(2)–C(3)	1·334 (6)	1·364 (6)
C(3)–N(4)	1·356 (5)	1·350 (6)
N(4)–C(5)	1·345 (5)	1·320 (5)
N(4)–C(6)	1·418 (5)	1·425 (5)
C(6)–C(7)	1·267 (7)	1·261 (7)
N(1)–Co–Cl	88·8 (3)	87·4 (3)
Co–N(1)–C(2)	128·7 (3)	127·2 (3)
Co–N(1)–C(5)	127·0 (3)	128·0 (3)
C(2)–N(1)–C(5)	104·3 (3)	104·2 (3)
N(1)–C(2)–C(3)	110·5 (4)	108·7 (4)
C(2)–C(3)–N(4)	106·6 (4)	107·0 (4)
C(3)–N(4)–C(5)	105·8 (3)	106·0(3)
N(1)–C(5)–N(4)	112·7 (4)	114·1 (4)
C(3)–N(4)–C(6)	130·0 (4)	129·5 (4)
C(5)–N(4)–C(6)	124·2 (4)	124·6 (4)
N(4)–C(6)–C(7)	125·0 (6)	125·4 (7)

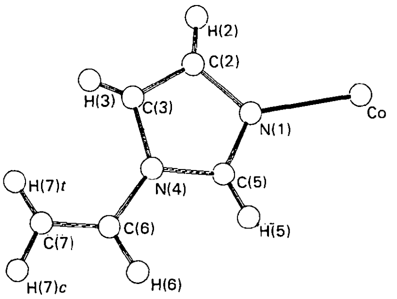

Fig. 1. Atomic numbering of the ligand in [Co(viz)$_4$]Cl$_2$.

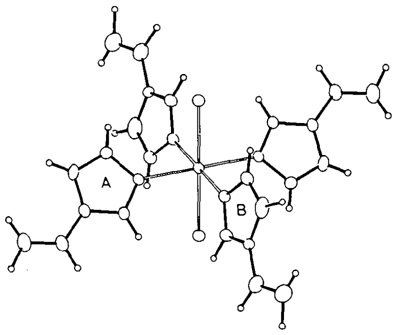

Fig. 2. *ORTEP* projection (Johnson, 1965) of [Co(viz)$_4$]Cl$_2$. Thermal ellipsoids are at the 50% probability level.

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