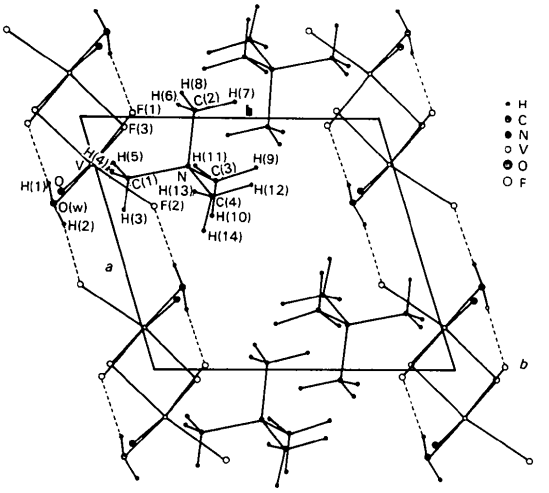

Fig. 1. Schematic structure of $[N(CH_3)_4][VOF_3(H_2O)]$ viewed along **c**.

The tetramethylammonium ions and the dimeric units are held together by a three-dimensional network of hydrogen bonds. The magnetic behaviour of $[N(CH_3)_4][VOF_3(H_2O)]$ will be analysed in terms of binuclear magnetic units such as $Cs_3V_2O_2F_7$ which contains similar groups (Darriet, Bonjour, Beltran-Porter & Drillon, 1984).

References

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Darriet, J., Bonjour, E., Beltran-Porter, D. & Drillon, M. (1984). *J. Magn. Mater.* **44**, 287–291.

Rabardel, L., Pouchard, M. & Hagenmuller, P. (1971). *Mater. Res. Bull.* **6**, 1325–1336.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Simonov, V. I. & Bukvetsky, B. V. (1978). *Acta Cryst.* B**34**, 355.

Waltersson, K. (1978). *Cryst. Struct. Commun.* **7**, 507–508.

Waltersson, K. (1979*a*). *J. Solid State Chem.* **28**, 121–131.

Waltersson, K. (1979*b*). *J. Solid State Chem.* **29**, 195–204.

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Intramolecular Hydrogen Bonding in Dichlorotetrakis(pyrazole-N^2)nickel(II) as Studied by Low-Temperature Neutron Diffraction, X-ray Diffraction and Infrared Spectroscopy

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Abstract. $[NiCl_2(C_3H_4N_2)_4]$, $M_r = 401{\cdot}9$, monoclinic, $C2/c$, $Z = 4$. (I) $T = 100$ K, $a = 13{\cdot}857\,(6)$, $b = 9{\cdot}182\,(5)$, $c = 14{\cdot}096\,(8)$ Å, $\beta = 117{\cdot}10\,(4)^\circ$, $V = 1596{\cdot}7\,(9)$ Å^3, $D_x = 1{\cdot}67$ g cm^{-3}, $\lambda = 1{\cdot}304$ Å, $\mu = 2{\cdot}31$ cm^{-1}, $F(000) = 9{\cdot}52$, final $R = 0{\cdot}036$ for 1771 neutron data. (II) $T = 295$ K, $a = 13{\cdot}881\,(4)$, $b = 9{\cdot}255\,(4)$, $c = 14{\cdot}417\,(8)$ Å, $\beta = 116{\cdot}85\,(3)^\circ$, $V = 1652{\cdot}4\,(1)$ Å^3, $D_x = 1{\cdot}62$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 15{\cdot}17$ cm^{-1}, $F(000) = 824$, final $R = 0{\cdot}028$ for 2210 X-ray data. The structural results of the X-ray and neutron studies agree well with each other and with a previous structure determination [Reimann, Mighell & Mauer (1967). *Acta Cryst.* **23**, 135–141]. Ni—N, 2·09 Å, and Ni—Cl distances, 2·50 Å, are in agreement with the tetragonal ligand-field spectra. The long Ni—Cl distances correspond to strong N—H···Cl interactions, N···Cl 3·09–3·12 Å. H-atom positions determined by neutron diffraction confirm the presence of these hydrogen bonds (H···Cl = 2·31–2·36 Å).

Introduction. An early structure determination of the title compound (Reimann, Mighell & Mauer, 1967) showed that an unusually long Ni—Cl bond occurs in comparison with other NiN_4Cl_2 chromophores. This long Ni—Cl contact was attributed to hydrogen bonding between the Cl^- ions and N—H groups of two pyrazole ligands (Reimann, 1969). Infrared spectra of related compounds, M(5-methylpyrazole)$_4X_2$ (M = metal, X = Cl, Br), strongly indicated that relatively strong hydrogen bonding is indeed responsible for the long Ni—X bonds and – as a consequence – the weak axial ligand field (Reedijk, 1970). However, a detailed study was not possible because the positions of the H

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atoms could not be determined accurately. Therefore, large single crystals have been grown for a neutron diffraction study. The crystals were checked by X-ray analysis (at room temperature) to ensure that the quality was sufficient to allow a low-temperature neutron diffraction study and to find out whether more accurate data could be expected.

The present paper describes the two structure determinations and compares them with the early data of Reimann *et al.* (1967). The geometries of the hydrogen bonds are compared with the infrared spectra of the N—H group, using the correlation first observed by Bellamy & Owen (1969).

Experimental. Large single crystals (up to 3 × 4 × 3 mm) were obtained from Ni(pyrazole)$_4$Cl$_2$ [synthesized according to Reimann *et al.* (1967)] by crystallization from EtOH/CH$_3$CN upon slow evaporation. An irregularly shaped crystal, volume about 26 mm^3, was used for neutron diffraction, while from the same batch a crystal approximately 0·55 × 0·45 × 0·50 mm was taken for X-ray diffraction.

I. *Neutron diffraction*

Data collected at 100 K using an He-flow cryostat (Herbert & Campbell, 1977) on a four-circle diffractometer at the HFR reactor at Petten; wavelength $\lambda = 1{\cdot}304$ Å obtained after diffraction from the (220) planes of the copper crystals of a double monochromator; lattice parameters by fitting θ settings of 11 reflections in θ range 19 to 34°. $\omega/2\theta$ step scans (0·051° step^{-1}); for $\theta < 57°$ 1816 independent reflections were measured; index range h 0–17, k 0–11, l −18–16; 3 reference reflections were measured every 75 reflections and no significant variations were detected. Absorption coefficient, 2·31 cm^{-1}, determined experimentally. Absorption corrections made by *ABSORB* (Spek, 1983), transmission factors 0·53 to 0·60. Refinement by full-matrix least squares on F_o, with $|F_o| > 2\sigma(F_o)$ and weights $w = [\sigma(F_o) + 0{\cdot}01|F_o|]^{-2}$, where $\sigma(F_o)$ is the e.s.d. of F_o obtained from counting statistics; scattering lengths from Koester & Yelon (1982); starting set of atom parameters from Reimann *et al.* (1967); number of parameters refined 179 (scale factor, isotropic extinction parameter, positional and anisotropic thermal parameters of all atoms). Final $R = 0{\cdot}036$, $wR = 0{\cdot}041$, $S = 2{\cdot}3$; shift-to-e.s.d. ratio in final cycle <0·02; largest correction for extinction (yF_c), $y = 0{\cdot}55$.

II. *X-ray diffraction*

Data collected at 295 K using an Enraf–Nonius CAD-4 diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters by fitting to θ, ω, φ and κ settings of 24 reflections in θ range 10 to 12°. ω/θ scan; for $\theta < 30°$, 9593 reflections measured; index range h −19–19, k −13–13, l −20–20; 2538 independent; $R_{\text{int}} = 0{\cdot}028$; 2210 observed with $I > 2\sigma(I)$ and included in the refinement. 3 reference reflections were measured every 1·5 h and no significant variations were detected. Corrections for Lorentz and polarization effects and for absorption (transmission factors 0·86 to 0·96). Starting set of atom parameters from Reimann *et al.* (1967). Number of

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	X-ray				Neutron			
	x	y	z	B_{eq}	x	y	z	B_{eq}
Ni	0	0	0	2·38 (1)	0	0	0	1·14 (3)
Cl	758 (1)	−1600 (1)	−910 (1)	3·37 (2)	738 (1)	−1619 (1)	−934 (1)	1·45 (2)
Ring I								
N(1)	1447 (1)	−190 (1)	1373 (1)	2·73 (6)	1462 (1)	−176 (1)	1397 (1)	1·29 (3)
N(2)	1628 (1)	459 (2)	2269 (1)	3·56 (7)	1629 (1)	509 (1)	2301 (1)	1·49 (3)
C(1)	2616 (2)	127 (2)	3034 (2)	4·23 (9)	2614 (1)	197 (1)	3107 (1)	1·57 (4)
C(2)	3079 (1)	−777 (2)	2609 (2)	5·65 (10)	3113 (1)	−747 (1)	2702 (1)	1·76 (4)
C(3)	2334 (1)	−949 (2)	1575 (1)	3·64 (7)	2358 (1)	−943 (1)	1630 (1)	1·48 (4)
H(1)*	1096	1118	2359	7·52 (65)†	1020 (2)	1120 (3)	2303 (2)	2·97 (9)
H(2)*	2969	504	3827	7·86 (65)†	2871 (3)	666 (4)	3889 (2)	3·19 (10)
H(3)*	3870	−1262	2994	8·13 (68)†	3912 (3)	−1220 (4)	3123 (3)	3·83 (10)
H(4)*	2458	−1601	1022	5·40 (47)†	2425 (3)	−1584 (3)	1022 (2)	2·99 (10)
Ring II								
N(3)	559 (1)	1814 (1)	−467 (1)	2·77 (6)	551 (1)	1824 (1)	−485 (1)	1·33 (3)
N(4)	1123 (1)	1687 (2)	−1002 (1)	4·67 (8)	1159 (1)	1681 (1)	−997 (1)	2·16 (3)
C(4)	1350 (2)	2976 (2)	−1281 (2)	5·61 (12)	1384 (1)	2972 (1)	−1300 (1)	2·42 (5)
C(5)	910 (2)	3994 (2)	−917 (2)	4·41 (9)	895 (1)	4025 (1)	−968 (1)	1·91 (4)
C(6)	423 (1)	3223 (2)	−412 (1)	3·72 (8)	385 (1)	3252 (1)	−463 (1)	1·62 (4)
H(5)*	1357	735	−1176	8·85 (71)†	1342 (3)	661 (3)	−1120 (3)	4·45 (13)
H(6)*	1801	3169	−1713	7·00 (61)†	1858 (4)	3039 (4)	−1726 (4)	5·78 (16)
H(7)*	929	5148	−1001	8·78 (92)†	900 (3)	5184 (3)	−1079 (3)	3·78 (11)
H(8)*	−4	3712	−27	6·68 (76)†	−90 (3)	3636 (4)	−88 (3)	4·06 (12)

* For the X-ray case the coordinates were fixed with respect to the parent atom.
† Isotropic temperature parameter.

parameters refined 115 (scale factor, isotropic extinction parameter, positional and anisotropic thermal parameters of non-H atoms, isotropic thermal parameters for H atoms). H-atom positions are locatable in difference Fourier maps, but calculated (N—H 1·01 Å, C—H 1·08 Å) and coupled to parent atoms. Full-matrix least squares based on F_o, $R = 0{\cdot}028$, $wR = 0{\cdot}037$, $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ based on counting statistics. Programs written or modified by E. W. M. Rutten-Keulemans and R. A. G. de Graaff. Scattering lengths and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); shift-to-e.s.d ratio in final cycle <0·1; max. and min. $\Delta\rho$ excursions in final difference synthesis 0·34 and 0·27 e Å^{-3}; largest correction for extinction (yF_c), $y = 0{\cdot}58$.

Discussion. Final atomic positions and equivalent isotropic thermal parameters are given in Table 1.* The numbering of the atoms is shown in Fig. 1. Bond distances and angles are collected in Table 2 together with the previous X-ray results (Reimann *et al.*, 1967). Comparison of the results from the three studies leads to the following observations:

(1) The Ni—Cl bonds appear to be slightly longer in the X-ray studies, which might originate from the lone-pair electrons on Cl$^-$.

(2) The C—C bonds in both pyrazole rings are longer in the neutron diffraction study which can be ascribed to the large difference in temperature factors between the two experiments.

(3) The corresponding bonds for the two pyrazole rings in the neutron experiment are more similar than those in the X-ray experiments.

(4) The hydrogen-bonding pattern is almost symmetric to both pyrazole N—H rings.

The geometry of the units Ni—Cl—H—N is such that H bonding seems to be optimized, through lengthening of the Ni—Cl bond (2·50 *vs* 2·40 Å according to the sum of the ionic radii), allowing Cl—H—N angles of about 130–135°. This hydrogen bonding is also seen from the IR spectra of the N—H group. The lowering from 3550 cm^{-1} in the gaseous ligand to 3300/3260 cm^{-1} would predict – according to the Bellamy–Owen (1969) relationship – N···Cl contacts of 3·24 and 3·20 Å. These distances are slightly larger than the N···Cl contacts from the neutron diffraction study (3·09 and 3·12 Å) at low temperature.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	X-ray	Neutron	Literature†
Ni—Cl	2·504 (1)	2·493 (1)	2·507 (1)
Ni—N(1)	2·095 (3)	2·091 (1)	2·097 (3)
Ni—N(3)	2·084 (1)	2·082 (1)	2·087 (3)
Cl···H(1^{i})	2·516*	2·364 (3)	
Cl···H(5)	2·408*	2·313 (4)	
Ring I			
N(1)—N(2)	1·342 (2)	1·343 (1)	1·345 (5)
N(2)—C(1)	1·351 (3)	1·351 (1)	1·357 (4)
C(1)—C(2)	1·358 (3)	1·384 (2)	1·371 (6)
C(2)—C(3)	1·387 (3)	1·404 (2)	1·393 (4)
N(1)—C(3)	1·331 (2)	1·333 (2)	1·329 (4)
N(2)—H(1)	1·01*	1·014 (4)	1·03*
C(1)—H(2)	1·08*	1·081 (4)	1·03*
C(2)—H(3)	1·08*	1·081 (3)	1·03*
C(3)—H(4)	1·08*	1·077 (4)	1·03*
N(2)···Cl^{i}	3·151 (1)	3·122 (1)	
Ring II			
N(3)—N(4)	1·330 (2)	1·341 (2)	1·342 (5)
N(4)—C(4)	1·341 (2)	1·345 (2)	1·333 (4)
C(4)—C(5)	1·351 (3)	1·379 (2)	1·356 (6)
C(5)—C(6)	1·393 (2)	1·403 (2)	1·389 (6)
N(3)—C(6)	1·326 (2)	1·334 (2)	1·321 (4)
N(4)—H(5)	1·01*	1·006 (4)	1·03*
C(4)—H(6)	1·08*	1·075 (7)	1·03*
C(5)—H(7)	1·08*	1·076 (3)	1·03*
C(6)—H(8)	1·08*	1·075 (5)	1·03*
N(4)···Cl	3·073 (2)	3·094 (1)	
Cl—Ni—N(1)	89·71 (4)	89·81 (3)	89·64
Cl—Ni—N(3)	90·07 (4)	90·36 (4)	90·30
N(1)—Ni—N(3)	91·98 (5)	91·64 (3)	91·96
Ni—Cl—H(1^{i})	79·38*	78·32 (9)	
Ni—Cl—H(5)	79·02*	77·11 (13)	
H(1^{i})—Cl—H(5)	90·33*	91·35 (12)	
Cl—H(5)—N(4)	124·85*	133·61 (41)	
Cl—H(1^{i})—N(2^{i})	122·24*	130·83 (23)	
Ring I			
N(2)—N(1)—C(3)	105·84 (14)	106·01 (8)	106·24 (24)
N(1)—N(2)—C(1)	111·30 (15)	111·71 (11)	111·06 (33)
N(2)—C(1)—C(2)	106·58 (17)	106·82 (11)	106·63 (32)
C(1)—C(2)—C(3)	106·27 (16)	104·91 (11)	105·81 (30)
N(1)—C(3)—C(2)	110·01 (16)	110·55 (12)	110·26 (35)
Ring II			
N(4)—N(3)—C(6)	104·98 (13)	105·44 (11)	104·91 (31)
N(3)—N(4)—C(4)	112·01 (15)	112·22 (12)	111·73 (37)
N(4)—C(4)—C(5)	107·19 (16)	106·76 (16)	107·40 (51)
C(4)—C(5)—C(6)	104·89 (14)	104·85 (12)	104·84 (34)
N(3)—C(6)—C(5)	110·91 (15)	110·73 (14)	111·13 (38)

Symmetry code: (i) $-x, -y, -z$.

* H position fixed with respect to parent atom.
† Reimann *et al.* (1967).

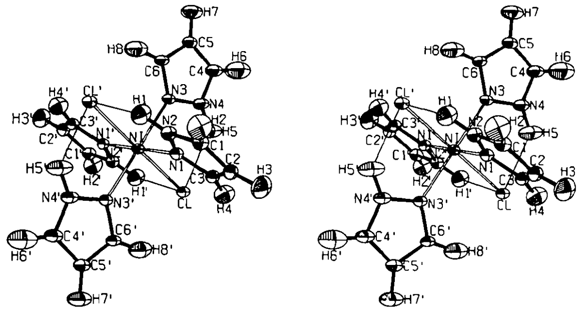

Fig. 1. Stereoscopic drawing (*ORTEP*II; Johnson, 1971) of the molecular structure of [NiCl$_2$(C$_3$H$_4$N$_2$)$_4$].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43335 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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References

Bellamy, L. J. & Owen, A. J. (1969). *Spectrochim. Acta Part A*, **25**, 329–333.

Herbert, I. R. & Campbell, S. J. (1977). *J. Appl. Cryst.* **10**, 18–20.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Koester, L. & Yelon, W. B. (1982). *Neutron Diffraction Newsletter*, December.

Reedijk, J. (1970). *Recl Trav. Chim. Pays-Bas*, **89**, 993–1016.

Reimann, C. W. (1969). *Chem. Commun.* pp. 145–146.

Reimann, C. W., Mighell, A. D. & Mauer, F. A. (1967). *Acta Cryst.* **23**, 135–141.

Spek, A. L. (1983). 8th Eur. Crystallogr. Meet., Liège. Abstracts.

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Structure of μ-Hydrido-bis(hydrido)bis(pentamethylcyclopentadienyl)bis(trimethylphosphino)diiridium Hexafluorophosphate

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Abstract. $[Ir_2(C_{10}H_{15})_2(C_3H_9P)_2H_3]PF_6$, $M_r = 955{\cdot}0$, monoclinic, $P2_1/n$, $a = 15{\cdot}2060\,(10)$, $b = 15{\cdot}0258\,(12)$, $c = 14{\cdot}6729\,(14)$ Å, $\beta = 99{\cdot}198\,(6)°$, $V = 3309{\cdot}4\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}917$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71073$ Å, $\mu = 81{\cdot}95$ cm^{-1}, $F(000) = 1840$, $T = 298$ K, $R = 0{\cdot}0185$ for 4324 unique reflections. The cation consists of a singly hydride-bridged Ir dimer with an unusually long Ir—Ir distance of 2·983 (1) Å. Each Ir is further coordinated to one pentamethylcyclopentadienyl ring, one trimethylphosphine and one terminal hydride.

Introduction. The reaction of the tris(μ-hydrido)bis(pentamethylcyclopentadienyl)diiridate cation with trimethylphosphine produces the title compound (Gilbert & Bergman, 1985). The starting dimer shows an unusually short Ir—Ir distance thought to be a metal—metal triple bond (Bau, Gellert & Shibu, 1975). Reaction with phosphine does not cleave the dimer, but rather produces the singly bridged hydride compound discussed here. No Ir dimer with a single bridge has yet been structurally characterized, consequently the Ir—Ir distance is of great interest.

Experimental. Crystal provided by Mr Thomas Gilbert, well-formed orange prism, 0·2 × 0·2 × 0·3 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; 24 reflections, $24 < 2\theta < 30°$, used to determine lattice parameters; ω–2θ-scan mode, variable scan rate 0·63–6·66° min^{-1} in 2θ; 4732 reflections in quadrant $\pm h$, $\pm k$, $+l$ ($h = -16$–16, $k = 0$–16, $l = 0$–15) measured with $3 < 2\theta < 45°$; three standard reflections (843, 3,10,3, $\bar{3}38$) measured every hour of data collection showed an average decline in intensity of 2·9% over 73 h, orientation checked every 250 reflections and reoriented if angle deviated by 0·1°; data corrected for background, scan speed, Lorentz and polarization factors; analytical absorption correction applied, transmission factors 0·184 to 0·245; systematically absent reflections and redundant data rejected yielding 4324 data, 3724 of which had $I > 3\sigma(I)$; six additional reflections rejected whose (Δ/σ) values were three times higher than average values, leaving 3718 reflections used in refinement.

Ir atoms located by Patterson technique, standard Fourier methods yielded all non-H atoms and the three hydride atoms; positional and anisotropic thermal parameters for all non-H atoms refined, positional and isotropic thermal parameters refined for hydrides, methyl-H atoms placed and refined with fixed thermal parameters; secondary-extinction correction applied, based on F_o/F_c for several low-angle reflections, final value after refinement, $6{\cdot}2\,(2) \times 10^{-8}$ e^{-2}; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = [4F_o^2/\sigma^2(F_o)^2]\sigma^2(F_o)^2 = \sigma_o^2(F_o^2) + (pF^2)^2$, $p = 0{\cdot}02$; final least-squares cycle

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