membered rings. For compounds with only a different central ring size, the coordinated bond lengths in Cu^{II} complexes with *N,N'*-bis(β-carbamoylethyl)ethylenediamine, which has a five-membered central ring, are shorter than those in {aqua[*N,N'*-bis(β-carbamoylethyl)trimethylenediamine]perchlorato}copper(II) perchlorate monohydrate, which has a six-membered central ring. Their stability constants are 12·58 and 10·27 respectively.

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The Structure of the Tetrahydrofuran Solvate of Tetrakis(2,6-diisopropylphenylisocyanide)nickel(II) Diperchlorate

By J. A. Kanters, H. L. L. M. Nijs and P. van der Sluis

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3,
Padualaan 8, 3584 *CH Utrecht, The Netherlands*

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Abstract. $[Ni(C_{13}H_{17}N)_4](ClO_4)_2.(C_4H_8O)_2$, $M_r = 1151·1$, *Pbca*, $a = 15·910\,(9)$, $b = 21·042\,(9)$, $c = 19·149\,(12)$ Å, $V = 6411\,(6)$ Å^3, $Z = 4$, $D_x = 1·192$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 4·4$ cm^{-1}, $F(000) = 2456$, $T = 295$ K. The structure has been refined to $R = 0·079$ for 3055 unique reflections with $I \geq 2·5\sigma(I)$. The nickel complex is centrosymmetric with Ni lying on a centre of inversion. The coordination geometry is approximately square-planar about Ni. The Ni—C bonds are almost perpendicular, 92·2 (3)°. The isocyanide ligands are essentially linear with angles of 174·0 (7) and 174·3 (7)° respectively.

Introduction. Isocyanides polymerize under the catalytic action of nickel(II) salts (Drenth & Nolte, 1979; Millich, 1980). Poly(isocyanides) have a rigid helical structure and, therefore, are chiral. In the past a mechanism has been proposed for the polymerization of isocyanides, catalysed by nickel(II). It was concluded that the polymerization is initiated by a nucleophilic attack on a coordinated isocyanide and proceeds *via* a series of consecutive insertion reactions around the Ni^{II} centre (Drenth & Nolte, 1979; Nolte, Zwikker, Reedijk & Drenth, 1978). However, intermediates of the polymerization reaction could not be isolated. Now we have been able to isolate and characterize the first intermediate, *i.e.* a square-planar nickel(II) isocyanide complex. The molecular and crystal structure of tetrakis(2,6-diisopropylphenylisocyanide)nickel(II) perchlorate is described, which is, as far as we know, the first X-ray analysis of a nickel(II) isocyanide complex. The scarce knowledge of nickel(II) isocyanide complexes can be ascribed to the high catalytic activity of Ni^{II} with respect to the polymerization of isocyanides.

Experimental. Crystals were obtained by slow cooling of a solution in tetrahydrofuran (THF) from room temperature to 253 K in a Dewar flask. Because of the extreme sensitivity to oxygen and the rapid deterioration in a solvent-free atmosphere, the crystals had to be sampled in a nitrogen atmosphere saturated with THF.

A yellow rod-shaped crystal (0·7 × 0·5 × 0·4 mm) was sealed under nitrogen in a capillary of Lindemann glass. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo *Kα* radiation. Cell dimensions were obtained

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Table 1. *Fractional atomic coordinates and (equivalent) isotropic thermal parameters* (Å^2) *for non*-H *atoms, with e.s.d.'s in parentheses*

	x	y	z	U_{eq}/U_{iso}
Ni	0·0000	0·0000	0·0000	0·0399 (3)
N(1)	−0·1630 (4)	0·0533 (3)	0·0496 (3)	0·054 (2)
N(2)	0·0161 (3)	0·0889 (3)	−0·1212 (3)	0·054 (2)
C(1)	−0·1006 (5)	0·0336 (3)	0·0281 (3)	0·052 (3)
C(2)	0·0057 (4)	0·0536 (3)	−0·0757 (3)	0·054 (3)
C(11)	−0·2382 (4)	0·0732 (3)	0·0820 (4)	0·054 (3)
C(12)	−0·2340 (5)	0·0931 (3)	0·1516 (4)	0·060 (3)
C(13)	−0·3089 (5)	0·1093 (3)	0·1823 (4)	0·068 (3)
C(14)	−0·3823 (5)	0·1078 (4)	0·1475 (4)	0·078 (4)
C(15)	−0·3851 (5)	0·0886 (4)	0·0779 (4)	0·073 (3)
C(16)	−0·3129 (5)	0·0712 (4)	0·0430 (4)	0·066 (3)
C(21)	0·0350 (5)	0·1342 (4)	−0·1721 (4)	0·060 (3)
C(22)	0·0982 (5)	0·1776 (4)	−0·1570 (4)	0·075 (3)
C(23)	0·1170 (6)	0·2224 (4)	−0·2084 (5)	0·104 (4)
C(24)	0·0768 (7)	0·2229 (5)	−0·2697 (5)	0·108 (5)
C(25)	0·0130 (7)	0·1799 (4)	−0·2828 (4)	0·105 (4)
C(26)	−0·0097 (6)	0·1331 (4)	−0·2347 (4)	0·074 (3)
C(121)	−0·1510 (5)	0·0957 (4)	0·1907 (4)	0·077 (3)
C(122)	−0·1430 (6)	0·0389 (5)	0·2384 (5)	0·137 (5)
C(123)	−0·1416 (6)	0·1561 (5)	0·2325 (5)	0·140 (5)
C(161)	−0·3127 (5)	0·0487 (5)	−0·0332 (4)	0·083 (4)
C(162)	−0·3721 (7)	−0·0067 (5)	−0·0449 (5)	0·153 (6)
C(163)	−0·3378 (8)	0·1055 (5)	−0·0795 (5)	0·149 (6)
C(221)	0·1425 (5)	0·1739 (4)	−0·0842 (5)	0·089 (4)
C(222)	0·1733 (6)	0·2397 (5)	−0·0607 (5)	0·138 (6)
C(223)	0·2142 (6)	0·1256 (5)	−0·0891 (5)	0·129 (5)
C(261)	−0·0782 (6)	0·0851 (4)	−0·2467 (4)	0·093 (4)
C(262)	−0·0848 (6)	0·0631 (4)	−0·3226 (5)	0·122 (5)
C(263)	−0·1609 (7)	0·1109 (5)	−0·2240 (5)	0·154 (6)
Cl	−0·1149 (2)	−0·0967 (1)	−0·1213 (1)	0·0868 (9)
O(1)	−0·0668 (3)	−0·1054 (3)	−0·0630 (2)	0·206 (5)
O(2)	−0·0639 (3)	−0·0908 (4)	−0·1784 (2)	0·226 (6)
O(3)	−0·1670 (3)	−0·1476 (2)	−0·1302 (3)	0·179 (4)
O(4)	−0·1618 (4)	−0·0427 (2)	−0·1140 (4)	0·298 (8)
O(31)	0·4235 (9)	0·2643 (6)	−0·0183 (7)	0·359 (8)†
C(32)	0·3714 (8)	0·2497 (6)	0·0916 (6)	0·186 (5)†
C(33)	0·4043 (7)	0·1862 (6)	0·0639 (6)	0·169 (5)†
C(34)	0·3917 (8)	0·3002 (5)	0·0367 (6)	0·157 (5)†
C(35)	0·4368 (8)	0·1995 (6)	−0·0099 (6)	0·165 (5)†

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

† U_{iso}.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Ni–C(1)	1·831 (8)	Ni–C(2)	1·839 (6)
C(1)–N(1)	1·152 (10)	C(2)–N(2)	1·157 (9)
N(1)–C(11)	1·411 (9)	N(2)–C(21)	1·396 (10)
C(11)–C(12)	1·399 (11)	C(21)–C(22)	1·389 (12)
C(12)–C(13)	1·372 (11)	C(22)–C(23)	1·395 (12)
C(13)–C(14)	1·345 (11)	C(23)–C(24)	1·337 (14)
C(14)–C(15)	1·393 (11)	C(24)–C(25)	1·383 (15)
C(15)–C(16)	1·378 (11)	C(25)–C(26)	1·396 (12)
C(16)–C(11)	1·404 (10)	C(26)–C(21)	1·394 (11)
C(12)–C(121)	1·519 (11)	C(22)–C(221)	1·564 (12)
C(121)–C(122)	1·510 (13)	C(221)–C(222)	1·536 (13)
C(121)–C(123)	1·509 (13)	C(221)–C(223)	1·531 (13)
C(16)–C(161)	1·534 (11)	C(26)–C(261)	1·504 (13)
C(161)–C(162)	1·517 (14)	C(261)–C(262)	1·529 (12)
C(161)–C(163)	1·541 (14)	C(261)–C(263)	1·488 (14)

C(1)–Ni–C(2)	92·2 (3)		
Ni–C(1)–N(1)	176·0 (5)	Ni–C(2)–N(2)	174·0 (6)
C(1)–N(1)–C(11)	174·0 (7)	C(2)–N(2)–C(21)	174·3 (7)
N(1)–C(11)–C(12)	117·9 (6)	N(2)–C(21)–C(22)	117·4 (7)
N(1)–C(11)–C(16)	118·3 (7)	N(2)–C(21)–C(26)	118·6 (7)
C(11)–C(12)–C(13)	116·2 (7)	C(21)–C(22)–C(23)	116·9 (7)
C(12)–C(13)–C(14)	122·4 (7)	C(22)–C(23)–C(24)	121·5 (9)
C(13)–C(14)–C(15)	120·6 (7)	C(23)–C(24)–C(25)	120·4 (9)
C(14)–C(15)–C(16)	120·9 (7)	C(24)–C(25)–C(26)	122·1 (8)
C(15)–C(16)–C(11)	116·1 (7)	C(25)–C(26)–C(21)	115·1 (8)
C(16)–C(11)–C(12)	123·8 (7)	C(26)–C(21)–C(22)	124·0 (8)
C(11)–C(12)–C(121)	121·5 (7)	C(21)–C(22)–C(221)	118·6 (7)
C(13)–C(12)–C(121)	122·3 (7)	C(23)–C(22)–C(221)	124·5 (7)
C(11)–C(16)–C(161)	120·9 (7)	C(21)–C(26)–C(261)	120·8 (7)
C(15)–C(16)–C(161)	123·0 (7)	C(25)–C(26)–C(261)	124·1 (7)
C(12)–C(121)–C(122)	110·1 (7)	C(22)–C(221)–C(222)	111·1 (7)
C(12)–C(121)–C(123)	112·2 (7)	C(22)–C(221)–C(223)	108·3 (7)
C(122)–C(121)–C(123)	109·7 (7)	C(222)–C(221)–C(223)	112·3 (7)
C(16)–C(161)–C(162)	112·1 (7)	C(26)–C(261)–C(262)	113·5 (7)
C(16)–C(161)–C(163)	107·9 (8)	C(26)–C(261)–C(263)	110·6 (7)
C(162)–C(161)–C(163)	110·5 (8)	C(262)–C(261)–C(263)	109·1 (8)

from setting angles of 24 reflections ($8·3 \leq \theta \leq 13·1°$). Space group *Pbca* from observed extinctions. Intensity data of 8051 reflections ($2\theta_{max} = 55°$; $0 \leq h \leq 20$, $0 \leq k \leq 24$, $0 \leq l \leq 27$) with the Ω–2θ mode, $\Delta\Omega = (0·55 + 0·35\tan\theta)°$. Two reference reflections measured every hour (221: r.m.s.d. 14%; 201: r.m.s.d. 1·3%) showed no significant intensity decline over 112 h of X-ray exposure time. Applying $I \geq 2·5\sigma(I)$ resulted in 3055 unique reflections. The structure was solved by combined Patterson and direct methods using *SHELXS*86 (Sheldrick, 1986). Blocked full-matrix least-squares refinement on F of positional and anisotropic thermal parameters of all non-H atoms revealed deviating geometries of the ClO_4^- ion and tetrahydrofuran (THF), and, with the exception of the Cl atom, unrealistic anisotropic behaviour of the atoms of these residues. Attempts to find a satisfactory disorder model failed. Therefore, the ClO_4^- ion and THF were refined with geometric constraints, Cl—O 1·365 (5), O···O 2·231 (2) Å for ClO_4^-, and C—C 1·53 (1), C—O 1·39 (2) Å for THF. The H atoms were included in the refinement at calculated positions (C—H = 1·0 Å), and refined in the riding mode with two overall isotropic temperature factors, one for the H atoms of the isopropyl groups and one for those of the phenyl groups. Because of the large disorder, the THF atoms were refined isotropically and no H atoms were introduced. The final R value converged at 0·079, $wR = 0·081$, $w = 1/\sigma^2(F_o)$, $S = 3·7$. The relatively high R value is to be attributed to the disorder of the perchlorate ion and the THF solvent molecule. The two overall isotropic thermal parameters of the H atoms refined to 0·21 (1) and 0·10 (2) Å^2 respectively. The final $(\Delta/\sigma)_{max} = 0·059$, $(\Delta/\sigma)_{ave} = 0·009$. Final residual electron density $-0·46 < \Delta\rho < 0·76$ e Å^{-3} with several peaks near the THF residue. The scattering factors for non-H atoms were taken from Cromer & Mann (1968), those for H atoms from Stewart, Davidson & Simpson (1965), anomalous-dispersion factors from Cromer & Liberman (1970). Calculations were performed with *SHELX*76 (refinement) (Sheldrick, 1976) and the *EUCLID* package (geometry calculations and illustration) (Spek, 1982).

Discussion. The atomic coordinates of the non-H atoms with their equivalent isotropic thermal parameters are given in Table 1.* Bond distances and bond angles are given in Table 2. A perspective view of the complex

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* Lists of structure factors, anisotropic thermal parameters and the complete internal geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51288 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

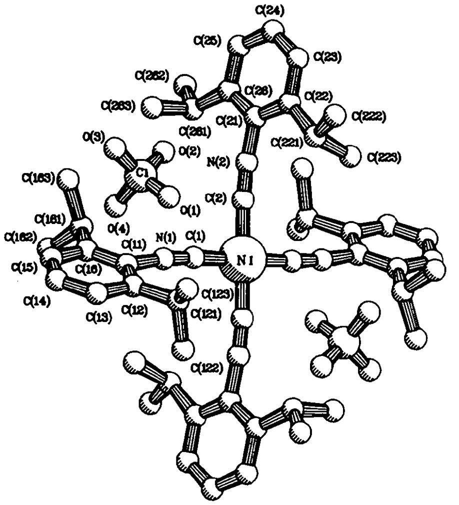

Fig. 1. Perspective view of the Ni complex with atom numbering. The solvate molecules have been omitted.

with atomic numbering is shown in Fig. 1. As Ni lies on an inversion centre, the coordinating isocyanide C atoms are coplanar with Ni, and the arrangement is approximately square-planar as follows from the C—Ni—C angle of 92·2 (3)°. The isocyanide ligands deviate from the C—Ni—C plane, the distances of N(1) and N(2) to this plane are 0·03 (1) and 0·10 (1) Å respectively and the Ni—C—N angles are 176·0 (5) and 174·0 (6)° respectively. The Ni—C distances [1·831 (8) and 1·839 (6) Å], the terminal N—C distances [1·152 (10) and 1·157 (9) Å] and the C—N—C angles [174·0 (7) and 174·3 (7)°] of the isocyanide ligands are similar to those observed in Ni^0 isocyanide complexes. In bis(*tert*-butylisocyanide)(azobenzene)nickel(0) (Dickson & Ibers, 1972) the corresponding values are 1·842 (5), 1·839 (5); 1·155 (6), 1·156 (6) Å and 175·3 (5), 177·5 (6)°, and in bis(*tert*-butylisocyanide)(*N*-*tert*-butyldicyanoketenimine)nickel(0) (Yarrow, Ibers, Tatsuno & Otsuka, 1973) the values are 1·819 (5), 1·876 (4); 1·149 (5), 1·147 (5) Å and 176·5 (4), 174·8 (4)°. The observed terminal C—N bond lengths lie in the range expected for C—N triple bonds. The N(1)—C(11) and N(2)—C(21) distances are 1·411 (9) and 1·396 (10) Å respectively and these are shorter than the corresponding distances in the Ni^0 complexes, where these distances involve C(sp^3) atoms. The angles between the phenyl rings and the C(1)—Ni—C(2) plane are 57·0 (4) ($C_{11}\to C_{16}$) and 71·9 (4)° ($C_{21}\to C_{26}$) respectively. The angle between the phenyl rings is 67·3 (4)°.

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A Tetracarbonyl(η^4-dienone)chromium Complex

By Stephen F. Pavkovic and Eugene J. Zaluzec

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626, *USA*

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Abstract. Tetracarbonyl[1–3,9a-η-(2,3-diethyl-4a,9a-dihydro-1-methoxy-4a,9-dimethyl-4H-carbazol-4-one)]-chromium(0), [Cr(CO)$_4$(C$_{19}$H$_{23}$NO$_2$)], $M_r = 461·4$, monoclinic, $P2_1/c$, $a = 15·2045$ (7), $b = 8·4622$ (3), $c = 17·3682$ (8) Å, $\beta = 92·28$ (1)°, $V = 2232·9$ (2) Å^3, $Z = 4$, $D_x = 1·37$ g cm^{-3}, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1·5418$ Å, $\mu = 45·5$ cm^{-1}, $F(000) = 960$, $T =$ 295 K. Refinement of 284 parameters based on 2472 observed intensities gave a final $R = 0·055$. The diene is π-bonded to Cr in this [Cr(dienone)(CO)$_4$] complex, and angles and average bond lengths from Cr to carbonyl C atoms *trans* to the diene are 100·9 (2)° and 1·842 (6) Å, and to the *cis*-carbonyl C atoms are 155·4 (2)° and 1·886 (7) Å. This is the first structure

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