Transition-metal Chemistry of Quinuclidinone-containing Ligands. Part V.[1] Crystal Structure of Dichloro[*trans*-2-(2-quinolyl)methylenequinuclidin-3-one]cobalt(II)

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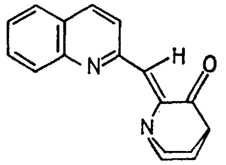
The crystal structure of the title compound has been determined from 2829 independent reflections measured by diffractometer. Crystals are triclinic, space group $P\bar{1}$, with the (non-conventional) unit-cell parameters, a = 9·492(4), b = 9·754(5), c = 9·243(5) Å, α = 89·91(5)°, β = 90·28(5)°, γ = 108·30(2)°, and Z = 2. The structure was solved by Patterson and Fourier techniques, and refined by full-matrix least-squares methods to R = 3·4%. The compound consists of cobalt(II) ions co-ordinated in a pseudotetrahedral manner to the two nitrogen donor atoms in the ligand and to the two chloride ions. The two Co–Cl distances are slightly different [2·219(1) and 2·227(1) Å], and the Co–N (quinoline) bond distance [2·014(2) Å] is somewhat shorter than Co–N (quinuclidinone) [2·064(2) Å]. The bond angles about Co are distorted from their pure tetrahedral value, the smallest being [100·35(9)°] the chelate 'bite' angle. The ligand is almost planar (excluding the two ethylene bridges), and the molecule therefore possesses an approximate mirror plane bisecting the Cl–Co–Cl angle.

DURING a study[2] of several bivalent first-row transition-metal complexes with *trans*-2-(2-quinolyl)methylenequinuclidin-3-one (I) (qnqn), two isomeric (yellow and violet) complexes of stoicheiometry [Ni(qnqn)Cl_2] were isolated. A detailed study[3] of the violet complex indicated that it is pseudotetrahedral. A similar study of the spectral and magnetic properties[3] and *X*-ray structure[1] of the yellow complex revealed that it is binuclear, containing two nickel(II) ions each in a five-co-ordinate, square pyramidal, geometry, and each sharing two bridging chlorine atoms. An additional study[4] of the thermal properties of the two nickel isomers revealed that these isomers can be interconverted by a unique, temperature-dependent, structural transformation.



(I)

Because crystals of the violet nickel complex sufficiently large for *X*-ray work could not be obtained, it was decided to determine the *X*-ray structure of the analogous [Co(qnqn)Cl_2] complex, which has many similar properties. Although their *X*-ray powder patterns are similar, the crystals of the two compounds are not isomorphous.[3]

EXPERIMENTAL

Preparation.—The [Co(qnqn)Cl_2] complex was prepared as described previously.[2] Single crystals were grown by slow evaporation of a methylene chloride solution. After *ca*. 3 weeks, a crop of green single crystals *ca*. 0·5 mm in their largest dimension were obtained. They were air stable.

Crystal Data.—$C_{17}H_{16}Cl_2CoN_2O$, M = 394, Triclinic, (non-conventional * unit-cell parameters) a = 9·492(2), b = 9·754(5), c = 9·243(5) Å, α = 89·91(5), β = 90·28(5), γ = 108·30(2)°, U = 812·4(9) Å^3, D_m (flotation) = 1·61(2), Z = 2, D_c = 1·611(3). Space group $P\bar{1}$. Mo-K_α radiation $\lambda(K_{\alpha1})$ = 0·70926, $\lambda(K_{\alpha2})$ = 0·71354Å; μ(Mo-K_α) = 0·63—0·87 cm^{-1}.

Data Collection.—A crystal *ca*. 0·2 × 0·3 × 0·4 mm was mounted with its long dimension, c^*, coincident with the spindle axis. Preliminary zero- and first-order precession photographs indicated the triclinic space group $P\bar{1}$ or $P1$. The crystal was then transferred to a Picker, four-circle, programmed diffractometer and 25 reflections were manually centred and used to refine, by a least-squares procedure,[5] accurate unit-cell parameters and crystal orientation.

Intensity data were obtained by a variable non-symmetric 2θ scan with a scan rate of 1·0° min^{-1}, made from 0·50° below to 0·50° above the 2θ setting; background was measured on both sides of the peak. The intensities of 3870 reflections were measured to 2θ = 52·5°. Niobium-filtered Mo-K_α radiation was used with a take-off angle of 2·0°. Attenuators were used to prevent the count rate at the detector from exceeding *ca*. 10^4 counts s^{-1}. Three standard reflections, measured at *ca*. 3 h intervals, revealed no instrument drift or crystal degradation.

Data Reduction.—The observed integrated intensities were corrected for background radiation, Lorentz-polarization effects, and absorption and were assigned standard deviations.[6] In order to determine whether the crystal was of space group $P1$ or $P\bar{1}$, the intensities of all (530) Friedel pairs were measured to 2θ = 25°, and a comparison resulted in an agreement factor of *ca*. 1·2% and indicated

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* All subsequent work was performed with this non-conventional unit cell. A Delauney reduction which used TRACERA indicated that the conventional unit cell was triclinic. The conventional cell indices and fractional co-ordinates can be obtained by using the following 3 × 3 matrix: −1,0,0; 0,1,0; 0,0,−1.

[1] Part IV, G. J. Long and E. O. Schlemper, *Inorg. Chem*., 1974, **13**, 279.

[2] D. L. Coffen and T. E. McEntee, jun., *J. Org. Chem*., 1970, **35**, 503.

[3] G. J. Long and D. L. Coffen, *Inorg. Chem*., 1974, **13**, 270.

[4] Part VI, G. J. Long, G. L. Bertrand, S. H. Wu, K. G. Mayhan, D. Noel, and D. L. Coffen, *J.C.S. Dalton*, in the press.

[5] All calculations were preformed on the IBM 360/65 computer of the University of Missouri-Columbia Computer Research Center, with the following programs: S. L. Lawton, TRACERA, Delauney reduction program; W. C. Hamilton, SORTH, sorting program; W. C. Hamilton and J. A. Ibers, NUPIK, Picker input program; W. C. Hamilton, HORSE, general adsorption program; R. Doedens and J. A. Ibers, NUCLS, least-squares program, a modification of W. Busing and H. Levy's program; A. Zalkin, FORDAP, Fourier program; W. Busing and H. Levy, ORFFE, function and error program; C. Johnson, ORTEP, thermal ellipsoid plot program; local data processing programs.

[6] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem*., 1967, **6**, 197.

space group $P\bar{1}$. Above $2\theta = 25°$, only reflections of positive l values were measured. Of the 3870 measured intensities, 3068 independent data points were obtained of which 2829 had $I > 2{\cdot}5\sigma(I)$, where $\sigma = [\sigma^2_{\text{counting}} + (0{\cdot}03F_0{}^2)^2]^{\frac{1}{2}}$.

Structure Determination and Refinement.—A straightforward interpretation of the Patterson map located the positions of the cobalt and two chlorine atoms. Full-matrix least-squares refinement of the positions of these atoms [minimizing the function $\Sigma w(|F_0|^2 - |kF_c|^2)^2$] converged with $R = 0{\cdot}612$ and $R' = 3{\cdot}03$ $\{R' = [\Sigma w(|F_0|^2 + |kF_c|^2)^2/\Sigma w(|F_0|^2)^2]^{\frac{1}{2}};\ w = 1/\sigma^2\}$. Subsequent, three-dimensional Fourier syntheses allowed the location of all the remaining non-hydrogen atoms. Three subsequent cycles of isotropic refinement of all non-hydrogen atoms gave $R = 0{\cdot}191$ and $R' = 0{\cdot}364$. Two cycles of anisotropic refinement of the cobalt and chlorine atoms and isotropic refinement of the remaining non-hydrogen atoms, including isotropic extinction and anomalous dispersion corrections, resulted in $R = 0{\cdot}111$ and $R' = 0{\cdot}228$. Scattering factors for non-hydrogen atoms were taken from ref. 7, with corrections for the effects of anomalous dispersion from ref. 8. Extinction corrections were made according to the method of Zachariasen.[9] Scattering factors for hydrogen were taken from ref. 10. Two subsequent cycles, in which all the non-hydrogen atoms were refined anisotropically, led to $R = 0{\cdot}075$ and $R' = 0{\cdot}155$. A difference-Fourier synthesis based on this refinement indicated 16 electron-density peaks (*ca.* 0·4 eÅ^{-3}) corresponding to the expected hydrogen-atom positions. Two final refinement cycles, in which all the non-hydrogen atoms were refined anisotropically and which included 16 hydrogen atoms, led to $R = 0{\cdot}044$ and $R' = 0{\cdot}106$. The final standard deviation of an observation of unit weight is 2·43. The final R is 0·034.

TABLE 1

Final positional and anisotropic thermal (×10^4) parameters for non-hydrogen atoms; here, and in subsequent Tables, estimated standard deviations are given in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	−0·06446(3)	0·15856(4)	−0·22806(4)	60·4(5)	107·3(5)	83·4(5)	10·9(4)	0·2(3)	−12·5(3)
Cl(1)	−0·18391(8)	0·2425(1)	−0·39708(8)	105(1)	248(2)	108(1)	74(1)	−12·0(8)	11·8(9)
Cl(2)	−0·16500(9)	−0·07603(8)	−0·1868(1)	125(1)	110(1)	222(2)	2·2(8)	12(1)	3(1)
N(1)	−0·0400(2)	0·2708(2)	−0·0417(2)	73(3)	94(3)	76(2)	17(2)	3(2)	−3(2)
N(2)	0·1545(2)	0·2051(2)	−0·2882(2)	71(3)	110(3)	97(3)	18(2)	−1(2)	−23(2)
O	0·5184(2)	0·4385(2)	−0·1897(3)	59(2)	183(3)	184(4)	5(2)	1(2)	−45(3)
C(1)	0·2303(3)	0·3604(3)	−0·0698(3)	69(3)	97(3)	96(3)	13(2)	−3(2)	−9(2)
C(2)	0·0925(3)	0·3430(3)	0·0116(3)	72(3)	84(3)	86(3)	20(2)	−4(2)	−6(2)
C(3)	0·1102(3)	0·4099(3)	0·1492(3)	94(4)	121(4)	98(3)	34(3)	−17(3)	−24(3)
C(4)	−0·0106(3)	0·3983(3)	0·2312(3)	117(4)	122(4)	88(3)	44(3)	7(3)	−10(3)
C(5)	−0·2848(3)	0·3136(3)	0·2551(3)	131(4)	143(4)	97(4)	54(3)	38(3)	9(3)
C(6)	−0·4192(3)	0·2475(4)	0·1948(3)	106(4)	165(5)	132(4)	43(4)	52(3)	13(4)
C(7)	−0·4314(3)	0·1864(4)	0·0563(3)	88(4)	171(5)	129(4)	18(3)	26(3)	−6(4)
C(8)	−0·3058(3)	0·1937(3)	−0·0220(3)	79(3)	161(4)	100(4)	15(3)	11(3)	19(3)
C(9)	−0·1640(3)	0·2629(3)	0·0377(3)	83(3)	93(3)	82(3)	21(3)	12(2)	6(2)
C(10)	−0·1530(3)	0·3250(3)	0·1772(3)	109(4)	97(3)	80(3)	40(3)	11(3)	4(2)
C(11)	0·2586(3)	0·3061(3)	−0·1931(3)	52(3)	90(3)	104(3)	11(2)	−4(2)	−5(2)
C(12)	0·4161(3)	0·3474(3)	−0·2471(3)	68(3)	125(4)	127(4)	27(3)	4(3)	−6(3)
C(13)	0·4265(3)	0·2640(4)	−0·3804(4)	70(4)	204(6)	163(5)	32(4)	16(3)	−56(4)
C(14)	0·3305(4)	0·3049(5)	−0·4936(4)	78(4)	370(9)	114(5)	20(5)	32(3)	−5(5)
C(15)	0·1710(3)	0·2706(4)	−0·4382(3)	81(4)	224(6)	79(3)	21(4)	14(3)	−3(3)
C(16)	0·3609(4)	0·1040(4)	−0·3451(6)	84(4)	173(5)	370(10)	42(4)	13(5)	−117(6)
C(17)	0·2000(3)	0·0693(3)	−0·2896(4)	96(4)	114(4)	239(6)	28(3)	−3(4)	−66(4)

Observed and calculated structure factors (×10) are listed in Supplementary Publication No. SUP 21170 (14 pp., 1 microfiche).* Final positional and anisotropic thermal parameters for non-hydrogen atoms are listed in Table 1, and the final positional parameters for hydrogen atoms in Table 2.

RESULTS AND DISCUSSION

The results of the structural analysis indicate that the molecule has pseudotetrahedral co-ordination about the cobalt ion. The co-ordination sphere contains two chloride ions and the two qnqn donor nitrogen atoms. The structure of the molecule and the atom numbering scheme are shown in Figure 1; details of the co-ordination sphere are shown in Figure 2. Intramolecular bond distances are given in Table 3, intramolecular bond angles in Table 4, equations and atomic deviations for several planes in the molecule in Table 5, root-

TABLE 2

Final positional parameters for hydrogen atoms *

Atom	x/a	y/b	z/c
H(1)	0·319	0·419	−0·022
H(3)	0·210	0·462	0·174
H(4)	0·007	0·443	0·319
H(5)	−0·273	0·359	0·339
H(6)	−0·505	0·241	0·246
H(7)	−0·522	0·137	0·014
H(8)	−0·315	0·150	−0·113
H(13)	0·533	0·296	−0·410
H(14)a	0·339	0·279	−0·585
H(14)b	0·369	0·422	−0·503
H(15)a	0·110	0·202	−0·500
H(15)b	0·139	0·351	−0·437
H(16)a	0·368	0·043	−0·436
H(16)b	0·422	0·079	−0·290
H(17)a	0·138	0·015	−0·353
H(17)b	0·183	0·018	−0·182

* Numbered according to the carbon atom to which they are attached.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[7] ' International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, p. 202, Table 3.3.1A.

[8] Ref. 7, p. 215, Table 3.3.2C.

[9] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

mean-square thermal displacements in Table 6, and all intermolecular contacts <3·8 Å in Table 7.

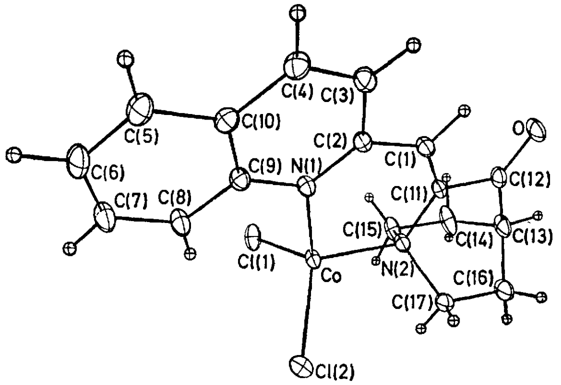

FIGURE 1 The structure of [Co(qnqn)Cl$_2$], showing the atom labelling

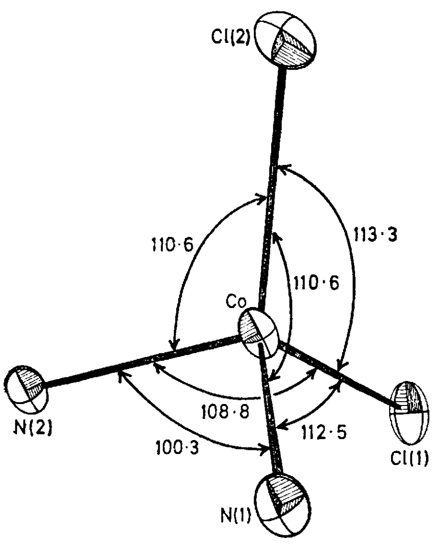

FIGURE 2 The details of the co-ordination about the cobalt ion including bond angles

TABLE 3

Intramolecular bond distances (Å)

Co–Cl(1)	2·227(1)	C(4)–C(10)	1·403(4)
Co–Cl(2)	2·219(1)	C(5)–C(10)	1·415(4)
Co–N(1)	2·014(2)	C(5)–C(6)	1·352(4)
Co–N(2)	2·064(2)	C(6)–C(7)	1·402(4)
O–C(12)	1·210(3)	C(7)–C(8)	1·373(4)
N(1)–C(2)	1·328(3)	C(8)–C(9)	1·412(4)
N(1)–C(9)	1·373(3)	C(9)–C(10)	1·414(4)
N(2)–C(11)	1·452(3)	C(11)–C(12)	1·504(4)
N(2)–C(15)	1·509(4)	C(12)–C(13)	1·498(4)
N(2)–C(17)	1·513(4)	C(13)–C(14)	1·517(5)
C(1)–C(2)	1·471(3)	C(13)–C(16)	1·521(6)
C(1)–C(11)	1·326(4)	C(14)–C(15)	1·531(4)
C(2)–C(3)	1·415(4)	C(16)–C(17)	1·545(5)
C(3)–C(4)	1·353(4)		

Although an individual molecule of [Co(qnqn)Cl$_2$] possesses no symmetry elements other than C_1, the molecule contains an approximate mirror plane of symmetry [plane (7) in Table 5]. The maximum deviation of any of the 17 constituent atoms from the plane is 0·229(3) Å for oxygen. Of the remaining atoms in the complex, the two chlorine atoms are the farthest from the plane [Cl(1) 1·869, Cl(2) 1·836 Å], and the four ethylene carbon atoms are very nearly symmetrically located with respect to it. A slight, but significant, difference is also observed in the two Co–Cl bond distances. The difference (0·008 Å) is four times the sum of the error associated with the two measurements, and is believed to be real. It is difficult to explain both this difference and the deviation from C_s symmetry on the basis of molecular effects. It is more likely that these differences arise from packing effects.

TABLE 4

Bond angles (°)

Cl(1)–Co–Cl(2)	113·31(6)	C(5)–C(6)–C(7)	120·6(3)
Cl(1)–Co–N(1)	112·52(7)	C(6)–C(7)–C(8)	120·6(3)
Cl(1)–Co–N(2)	108·75(8)	C(7)–C(8)–C(9)	120·0(3)
Cl(2)–Co–N(1)	110·56(8)	N(1)–C(9)–C(8)	119·4(2)
Cl(2)–Co–N(2)	110·59(7)	N(1)–C(9)–C(10)	121·5(2)
N(1)–Co–N(2)	100·35(9)	C(8)–C(9)–C(10)	119·0(2)
Co–N(1)–C(2)	122·1(2)	C(4)–C(10)–C(5)	123·0(2)
Co–N(1)–C(9)	118·8(2)	C(4)–C(10)–C(9)	117·9(2)
C(2)–N(1)–C(9)	118·9(2)	C(5)–C(10)–C(9)	119·1(3)
Co–N(2)–C(11)	114·1(2)	N(2)–C(11)–C(1)	127·5(2)
Co–N(2)–C(15)	108·1(2)	N(2)–C(11)–C(12)	112·8(2)
Co–N(2)–C(17)	110·8(2)	C(1)–C(11)–C(12)	119·6(2)
C(11)–N(2)–C(15)	107·8(2)	O–C(12)–C(11)	123·4(3)
C(11)–N(2)–C(17)	106·4(2)	O–C(12)–C(13)	125·6(3)
C(15)–N(2)–C(17)	109·6(2)	C(11)–C(12)–C(13)	111·0(2)
C(2)–C(1)–C(11)	133·4(2)	C(12)–C(13)–C(14)	105·8(3)
N(1)–C(2)–C(1)	121·9(2)	C(12)–C(13)–C(16)	107·8(3)
N(1)–C(2)–C(3)	122·0(2)	C(14)–C(13)–C(16)	109·5(3)
C(1)–C(2)–C(3)	116·1(2)	C(13)–C(14)–C(15)	109·9(3)
C(2)–C(3)–C(4)	119·7(2)	N(2)–C(15)–C(14)	111·7(3)
C(3)–C(4)–C(10)	120·0(2)	C(13)–C(16)–C(17)	110·6(2)
C(6)–C(5)–C(10)	120·6(3)	N(2)–C(17)–C(16)	110·3(3)

TABLE 5

(*a*) Equations of several least-squares planes in the form $Ax + By + Cz - D = 0$

Plane	*A*	*B*	*C*	*D*
(1) [a]	3·01	−8·89	3·77	−2·71
(2) [b]	3·21	−8·86	3·81	−2·70
(3) [c]	2·83	−8·94	3·68	−2·68
(4) [d]	3·25	−8·44	4·57	−2·59
(5)	3·90	−8·18	4·81	−2·43
(6)	3·69	−8·40	4·54	−2·51
(7)	3·41	−8·51	4·42	−2·58

(*b*) Deviations (Å) from least-squares planes

Plane (1): N(1) 0·023(2), C(2) −0·021(2), C(3) −0·043(3), C(4) 0·005(3), C(5) 0·022(3), C(6) −0·022(3), C(7) −0·038(3), C(8) −0·019(3), C(9) 0·018(3), C(10) 0·025(2)

Plane (2): N(1) 0·010(2), C(2) −0·003(2), C(3) −0·015(3), C(4) 0·013(3), C(9) −0·016(3), C(10) 0·002(2)

Plane (3): C(5) 0·008(3), C(6) −0·003(3), C(7) 0·003(3), C(8) 0·000(3), C(9) 0·003(2), C(10) −0·006(2)

Plane (4): Co −0·0002(3), N(1) −0·16(2), N(2) 0·043(2), C(1) −0·022(3), C(2) 0·046(2), C(11) −0·039(3)

Plane (5): O −0·048(3), N(2) −0·033(2), C(1) 0·045(3), C(11) 0·003(3), C(12) 0·024(3), C(13) 0·106(4)

Plane (6): O −0·119(3), N(1) −0·100(2), N(2) 0·051(2), C(1) 0·019(3), C(2) 0·023(2), C(3) 0·150(3), C(11) 0·017(3), C(12) 0·010(3), C(13) 0·145(4)

Plane (7): Co, 0·0010(3), N(1) −0·047(3), N(2) 0·085(2), O −0·229(3), C(1) −0·012(3), C(2) 0·023(2), C(3) 0·122(3), C(4) 0·172(3), C(5) 0·065(3), C(6) −0·096(3), C(7) −0·230(3), C(8) −0·210(3), C(9) −0·052(3), C(10) 0·074(2), C(11) −0·002(3), C(12) −0·053(3), C(13) 0·105(4)

[a] Quinolyl ring. [b] ' Pyridine ' ring. [c] ' Benzene ' ring. [d] Chelate ring.

All bond distances and angles are chemically reasonable and in good agreement with values for related compounds. The Co–Cl bond distances (2·227 and 2·219 Å) are in good agreement with those [11] for similar tetrahedral cobalt(II) chloride complexes and are only slightly shorter than the Ni–Cl(terminal) distance in $[\{Ni(qnqn)Cl_2\}_2]$.[1] The cobalt to aromatic amine nitrogen [N(1)] distance is significantly shorter than the cobalt to tertiary aliphatic amine [N(2)] distance, and this might result from either the differing pK_a values of the amines or from steric crowding about the tertiary amine. However, a study of the bond distances for related cobalt(II) aromatic amine and tertiary amine complexes failed to reveal any trends that would support the above rationalizations. The bond distances in the qnqn ligand are essentially the same in both $[Co(qnqn)Cl_2]$ and $[\{Ni(qnqn)Cl_2\}_2]$,[1] although the qnqn chelation angles in the two complexes are different. In the pseudotetrahedral cobalt complex, N(1)–Co–N(2) is 100·35(9)°, whereas in the square-pyramidal nickel complex N(1)–Ni–N (2) is reduced to 97·65(9)°. This difference indicates flexibility in the qnqn ligand and in part may account for its ability to form two isomers with Ni.[3]

TABLE 6

Root-mean-square thermal displacements (Å) along the directions of the principal axes

Atom	Min.	Med.	Max.
Co	0·156(1)	0·1854(7)	0·2314(6)
Cl(1)	0·185(1)	0·224(1)	0·330(1)
Cl(2)	0·196(1)	0·266(1)	0·311(1)
N(1)	0·168(3)	0·182(2)	0·212(3)
N(2)	0·171(4)	0·186(3)	0·242(3)
O	0·155(3)	0·251(3)	0·325(3)
C(1)	0·165(4)	0·202(3)	0·222(3)
C(2)	0·171(4)	0·190(3)	0·199(3)
C(3)	0·182(4)	0·204(4)	0·242(4)
C(4)	0·189(4)	0·219(4)	0·235(4)
C(5)	0·174(4)	0·241(4)	0·261(4)
C(6)	0·168(4)	0·265(4)	0·270(3)
C(7)	0·180(4)	0·239(4)	0·291(4)
C(8)	0·176(4)	0·204(4)	0·284(4)
C(9)	0·174(4)	0·200(4)	0·208(4)
C(10)	0·180(4)	0·199(4)	0·220(3)
C(11)	0·146(4)	0·206(3)	0·214(4)
C(12)	0·166(4)	0·229(4)	0·244(4)
C(13)	0·159(4)	0·233(4)	0·336(4)
C(14)	0·167(5)	0·234(5)	0·418(5)
C(15)	0·174(4)	0·201(4)	0·325(4)
C(16)	0·174(5)	0·232(4)	0·424(6)
C(17)	0·195(3)	0·204(4)	0·339(4)

TABLE 7

Intermolecular contact distances

Cl(2) · · · N(1)	3·758(3) [a]	Cl(2) · · · C(14)	3·741(5)
Cl(2) · · · C(1)	3·549(3) [a]	O · · · C(7)	3·487(5)
Cl(2) · · · C(2)	3·314(3) [a]	O · · · C(8)	3·655(4)
Cl(2) · · · C(3)	3·473(3) [a]	C(7) · · · C(7)	3·613(7)
Cl(1) · · · C(5)	3·484(4)	C(7) · · · C(8)	3·779(5)
Cl(1) · · · C(13)	3·773(3)	C(7) · · · C(12)	3·714(5)
Cl(2) · · · C(6)	3·772(4)		

[a] Between symmetry-related molecules in the same unit cell.

The thermal motion of some atoms (Table 6) is highly anisotropic with the minimum and maximum ellipsoidal axes differing by a factor of more than two. In contrast to the nickel complex,[1] the maximum vibration of the qnqn ligand in the cobalt complex corresponds to a twisting motion about two axes, coplanar with the planar portion of qnqn. One of these twist axes, approximately coincident with the C(11)–C(12) bond, affects the observed ellipsoidal shapes of the quinuclidinone ethylene carbon atoms. The other, approximately along the Co–N(1) bond direction, affects the vibration of atoms, such as C(6), C(7), and O. As frequently is observed, the minimum vibration of the cobalt bonded atoms is essentially in the bond direction.

As pointed out in a previous study [3] of the electronic properties of the metal complexes of qnqn, it is believed that the cobalt complex and the violet nickel complex are similar (although not identical) in structure. Because the violet $[Ni(qnqn)Cl_2]$ exhibits an unusual low-temperature [3] and high-pressure [12] structural conversion to its yellow $[\{Ni(qnqn)Cl_2\}_2]$ isomer, it is important to have some knowledge of the details of its bonding. Even though we were unable to obtain single crystals of violet $[Ni(qnqn)Cl_2]$ for *X*-ray study, the study of the chelation ring and the relative orientation of the two molecules of $[Co(qnqn)Cl_2]$ per unit cell has provided insight into the nature of the transformation between the two nickel isomers.

Figure 3 shows the relative orientation of the co-ordination spheres of the two cobalt molecules in the unit cell. The two cobalt atoms and the two Cl(2) atoms occupy non-bonding positions in close proximity to each other, whereas the two qnqn ligands are widely separated. It seems reasonable to propose a similar orientation in violet $[Ni(qnqn)Cl_2]$ but with a significantly shorter Ni · · · Cl(2) distance. Hence, the application of pressure [12] to violet $[Ni(qnqn)Cl_2]$ decreases the Ni · · · Cl(2) distances to the point where two additional bonds are formed irreversibly to yield $[\{Ni(qnqn)Cl_2\}_2]$.[3] The longer non-bonded distance in the cobalt complex may account for its failure to dimerise at high pressure (up to *ca.* 50 kbar).[13] A comparison of the density of the cobalt complex with that of the yellow nickel dimer indicates that a 3%

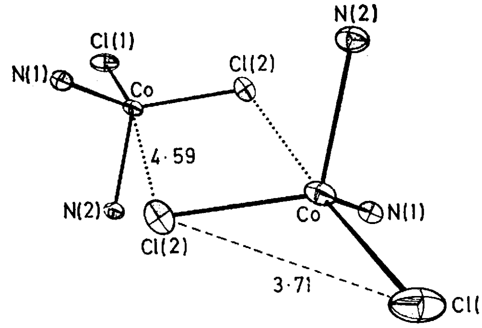

FIGURE 3 A perspective view of the orientation of the two cobalt co-ordination spheres in the unit cell

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[11] R. L. Carlin, *Transition Metal Chem.*, 1965, **1**, 1, and refs. therein.

[12] G. J. Long and J. R. Ferraro, *J.C.S. Chem. Comm.*, 1973, 719.

[13] G. J. Long and J. R. Ferraro, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 393.

decrease in volume would be required for this transformation.

A similar comparison of the chelation rings in $[Co(qnqn)Cl_2]$ and in $[\{Ni(qnqn)Cl_2\}_2]$ indicates some distinct differences. In the former, the chelation ring is almost planar with only a slight ' boat ' configuration. In the dimeric nickel complex[1] the chelation ring is much more highly distorted from planar geometry. Apparently, distinct changes in both the geometry of the chelation ring and the conformation of the ligand (compare plane (7), Table 5, with the analogous more highly distorted plane[1] in $[\{Ni(qnqn)Cl_2\}_2]$) occur as the bite angle of qnqn changes from 100·35° in the pseudotetrahedral cobalt complex to 97·65° in the square-pyramidal dimeric nickel complex. When the yellow dimeric complex, $[\{Ni(qnqn)Cl_2\}_2]$, is heated to *ca.* 230 °C the molecule has sufficient vibrational energy to break the two bridging chlorine bonds and to form the monomeric violet $[Ni(qnqn)Cl_2]$ complex (which we assume is similar to the cobalt complex). This complex would then have highly planar configurations for qnqn and the chelation ring which, upon cooling to room temperature, do not easily revert to the highly non-planar configurations observed in $[\{Ni(qnqn)Cl_2\}_2]$.[1] However, upon further cooling to *ca.* 195 K, the decrease in thermal vibrations and unit-cell size, and the accompanying changes in lattice packing, permit or force the change in the conformation of the qnqn molecule and the chelation ring and allows the reformation of the bridging Ni–Cl bonds.

It is interesting to contrast the structure of $[Co(qnqn)Cl_2]$ with those of pseudotetrahedral $[Zn(dmp)Cl_2]$, $[Co(dmp)Cl_2]$, and purple β-$[Ni(dmp)Cl_2]$ (dmp = 2,9-dimethyl-1,10-phenanthroline) reported by Preston and Kennard.[14] The $[Ni(dmp)Cl_2]$ complex also exists as an isomeric yellow square-pyramidal dimer, α-$[\{Ni(dmp)Cl_2\}_2]$,[15] which is very similar in structure to yellow $[\{Ni(qnqn)Cl_2\}_2]$. The zinc complex is rather similar to $[Co(qnqn)Cl_2]$ particularly with regard to its crystal morphology and co-ordination-sphere bond distances while the major difference occurs in the ' bite ' angle for the bidentate ligand. In $[Zn(dmp)Cl_2]$, the chelating bond angle is only 81·5°, whereas in $[Co(qnqn)Cl_2]$ it is 100·3°, a value more typical of tetrahedral co-ordination. Thus qnqn is a rather flexible ligand, whereas dmp is rather rigid in its chelation geometry. This difference in chelation rigidity in dmp and qnqn is, no doubt, related to the difference in the thermal properties of the isomers of $[Ni(qnqn)Cl_2]$ and $[Ni(dmp)Cl_2]$. As reported earlier,[16] yellow α-$[\{Ni(dmp)Cl_2\}_2]$ can be converted into purple β-$[Ni(dmp)Cl_2]$ by heating it to *ca.* 180 °C; however, unlike violet $[Ni(qnqn)Cl_2]$, the purple $[Ni(dmp)Cl_2]$ does not revert to its yellow dimeric isomer on cooling to liquid-nitrogen temperature.[17] The rigidity of the dmp ligand prevents the readjustment of the configuration of purple $[Ni(dmp)Cl_2]$ to one which would permit the formation of the dimer. In violet $[Ni(qnqn)Cl_2]$ the flexibility of qnqn, when required by crystal packing effects at low temperature, does permit the formation of the dimeric yellow complex.

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