Structure of Bis[dichloro-μ-bis(3,5-dimethyl-4-pyrazolyl)methane-cobalt(II)]–Ethanol (3:2), $C_{22}H_{32}Cl_4Co_2N_8.\frac{2}{3}C_2H_6O$
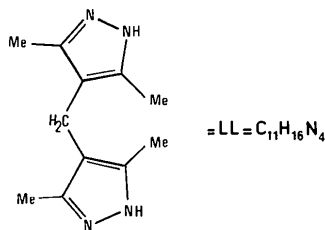
By C. Foces-Foces, F. H. Cano and S. García-Blanco

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, Madrid-6, Spain

Abstract. $M_r = 698.9$, triclinic, $P\bar{1}$, $a = 20.254$ (2), $b = 12.750$ (2), $c = 9.649$ (1) Å, $\alpha = 103.91$ (1), $\beta = 92.58$ (1), $\gamma = 104.23$ (1)°, $Z = 3$, $V = 2330.1$ (5) Å³, $D_x = 1.494$ Mg m⁻³, $\lambda(Cu\,K\bar{\alpha}) = 1.5418$ Å, $\mu = 12.29$ mm⁻¹, $F(000) = 1078$, $T = 295$ K. Final $R = 0.080$ for 4035 observed reflexions. The structure consists of dimers of the title formula (one of them crystallographically centrosymmetric), with two tetrahedral Co atoms per dimer. The three dimers present in the unit cell have different conformations; two have pseudo $\bar{4}2m$ symmetry and the other pseudo $2/m$ symmetry. They pack, together with the ethanol molecule, in a network determined by hydrogen interactions.

Introduction. The ligand used in this complex belongs to a series of 4,4′-substituted bipyrazole derivatives synthesized by Cuadro, Elguero & Navarro (1981), some of them presenting cytostatic activity. The complexing capacity of these ligands with transition metals, such as Co^{II}, Ni^{II} and Rh^{I}, is being studied in the Institute of Medicinal Chemistry (CSIC, Madrid) (Roger, Santos, Cuadro, Elguero & Navarro, 1982; Uson, Oro, Esteban, Cuadro, Elguero & Navarro, 1982).

$= LL = C_{11}H_{16}N_4$

The crystal analysis of the title compound was undertaken to determine whether the complex is present as single molecules, oligomeric groups or polymeric chains.

Experimental. Crystal size 0.40–0.06 mm. Philips PW1100 four-circle diffractometer, graphite-monochromated Cu $K\alpha$, $\omega/2\theta$ scan mode. Lattice parameters measured by least-squares from 41 reflections with $\theta < 38°$. Irregular crystal shape prevented any correction for absorption being made. 6898 independent

reflexions up to $\theta < 60°$. Range of hkl $\overline{23},\overline{14},0$ to 23,14,11. Two standard reflexions measured every 90 min showed no variation in intensity. 4035 observed reflexions with $I > 3\sigma(I)$. Structure solved by Patterson analysis. Structure refined by block-diagonal least-squares on observed F's with partial contribution;* 513 non-H parameters refined (coordinates and anisotropic temperature factors), 201 H parameters refined (coordinates and isotropic temperature factors) [in ethanol molecule all H-atom thermal factors kept fixed as well as coordinates (6) of H(31A) and H(32A)]. Final $R = 0.080$, $R_w = 0.095$; empirical weighting scheme giving no trends in $\langle w\Delta^2F\rangle$. Anomalous-dispersion corrections for Co and Cl from *International Tables for X-ray Crystallography* (1974). Calculations performed with XRAY70 (Stewart, Kundell & Baldwin, 1970) and programs *PARST* (Nardelli, 1982) and *PESOS* (Martínez-Ripoll & Cano, 1975) on a Univac 1108 computer.

Discussion. The structure consists of two independent dimers of $Cl_2Co(LL)$, in a network of hydrogen interactions involving the ethanol molecule (see Fig. 1). The unit-cell content can be written as $[Co^{II}Cl_2(LL)]_2.\frac{2}{3}C_2H_5OH$ with a dimer being crystallographically centrosymmetric. δR_w(obs) analysis (Abrahams & Keve, 1971), comparing weighted F_o vs F_c, showed the consistency of the weighting scheme used. Final positional parameters and the geometrical characteristics of the complex are given in Tables 1 and 2, and the atomic numbering is presented in Fig.1.†

---

* The partial contribution refers to the facility of refinement in the XRAY system where the F_c are separated into two parts $F_{c1} + F_{c2}$; only the parameters involved in F_{c1} are refined, F_{c2} being calculated and added to F_{c1} as a 'partial contribution'. In the present work the separation is F_c(non-H's) + F_c(H's) and as a 'partial contribution' we use alternately in successive cycles F_c(non-H's) and then F_c(H's).

† Lists of structure factors, anisotropic thermal parameters, hydrogen fractional coordinates, δR_w(obs) full-normal-probability-plot parameters, statistics of the geometry of the complex, the main torsion angles and main dihedral angles between planar parts of the complex have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38489 (53 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for the heavy atoms*

$$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j\cos(a_i,a_j).$$

	x	y	z	U_{eq} (Å² ×10³)
C(31)	−0·061 (4)	−0·598 (3)	−0·212 (9)	372 (53)
C(32)	−0·130 (3)	−0·633 (5)	−0·211 (6)	249 (34)
O	−0·034 (2)	−0·497 (5)	−0·152 (6)	354 (39)
Co(1)	0·3951 (1)	0·0166 (1)	0·1013 (2)	35 (1)
Cl(1)	0·4680 (1)	0·1470 (2)	0·0203 (3)	46 (1)
Cl(2)	0·4377 (2)	−0·0301 (3)	0·2877 (3)	56 (1)
N(1)	0·3650 (4)	−0·1065 (8)	−0·0809 (10)	37 (4)
N(2)	0·3950 (4)	−0·1034 (8)	−0·0228 (10)	39 (4)
C(3)	0·3662 (5)	−0·1910 (9)	−0·3126 (12)	35 (4)
C(4)	0·3105 (5)	−0·2570 (9)	−0·2625 (12)	39 (5)
C(5)	0·3125 (5)	−0·2014 (9)	−0·1177 (13)	36 (5)
C(6)	0·2607 (6)	−0·3644 (9)	−0·3465 (13)	49 (5)
C(7)	0·3890 (6)	−0·2044 (11)	−0·4589 (14)	55 (5)
C(8)	0·2674 (6)	−0·2319 (10)	−0·0100 (14)	51 (5)
N(2′)	0·0771 (4)	−0·4011 (8)	−0·3239 (12)	48 (4)
N(1′)	0·0912 (5)	−0·3020 (7)	−0·3664 (11)	48 (4)
C(5′)	0·1582 (6)	−0·2765 (9)	−0·3782 (15)	50 (5)
C(4′)	0·1867 (6)	−0·3583 (9)	−0·3439 (13)	44 (5)
C(3′)	0·1335 (6)	−0·4341 (9)	−0·3105 (13)	40 (5)
C(8′)	0·1931 (7)	−0·1708 (12)	−0·4198 (18)	75 (7)
C(7′)	0·1307 (7)	−0·5402 (11)	−0·2653 (20)	75 (7)
Co(2)	0·3494 (1)	0·2776 (2)	0·6733 (2)	42 (1)
Cl(11)	0·3539 (2)	0·0993 (2)	0·6347 (3)	51 (1)
Cl(12)	0·2675 (2)	0·3412 (3)	0·7859 (4)	69 (2)
N(11)	0·4423 (5)	0·3646 (8)	0·7708 (10)	43 (4)
N(12)	0·4922 (5)	0·3157 (8)	0·7972 (11)	45 (4)
C(13)	0·5556 (6)	0·3903 (9)	0·8279 (13)	42 (5)
C(14)	0·5450 (5)	0·4915 (9)	0·8191 (11)	34 (4)
C(15)	0·4757 (5)	0·4739 (9)	0·7857 (12)	39 (4)
C(16)	0·6001 (5)	0·6025 (9)	0·8472 (12)	39 (4)
C(17)	0·6162 (6)	0·3562 (11)	0·8665 (15)	55 (6)
C(18)	0·4332 (6)	0·5522 (10)	0·7653 (16)	58 (6)
N(12′)	0·7086 (4)	0·6366 (7)	0·5559 (11)	42 (4)
N(11′)	0·6576 (5)	0·6761 (7)	0·5125 (11)	43 (4)
C(15′)	0·6119 (5)	0·6670 (8)	0·6057 (11)	32 (4)
C(14′)	0·6352 (6)	0·6236 (8)	0·7148 (12)	35 (4)
C(13′)	0·6986 (5)	0·6071 (9)	0·6819 (12)	38 (4)
C(18′)	0·5481 (6)	0·7046 (11)	0·5924 (14)	53 (6)
C(17′)	0·7483 (6)	0·5667 (11)	0·7587 (16)	60 (6)
Co(3)	0·0201 (1)	−0·2174 (1)	−0·3706 (2)	49 (1)
Cl(21)	0·0169 (2)	−0·1498 (3)	−0·5655 (4)	79 (2)
Cl(22)	−0·0761 (2)	−0·3393 (3)	−0·3480 (5)	94 (2)
N(21)	0·0509 (5)	−0·0775 (7)	−0·2081 (12)	47 (4)
N(22)	0·0563 (5)	0·0263 (7)	−0·2285 (11)	45 (4)
C(23)	0·0873 (5)	0·1075 (8)	−0·1061 (13)	35 (4)
C(24)	0·1012 (5)	0·0537 (9)	−0·0060 (12)	39 (5)
C(25)	0·0774 (6)	−0·0605 (9)	−0·0737 (14)	44 (5)
C(26)	0·1349 (6)	0·1052 (10)	0·1428 (13)	51 (5)
C(27)	0·0998 (7)	0·2293 (9)	−0·0989 (15)	57 (5)
C(28)	0·0778 (8)	−0·1574 (12)	−0·0083 (17)	68 (7)
N(22′)	0·2873 (5)	0·0507 (8)	0·2978 (10)	41 (4)
N(21′)	0·3081 (5)	0·0562 (8)	0·1638 (9)	39 (4)
C(25′)	0·2566 (6)	0·0778 (10)	0·0940 (13)	43 (5)
C(24′)	0·2030 (5)	0·0848 (8)	0·1781 (12)	35 (4)
C(23′)	0·2233 (5)	0·0683 (9)	0·3080 (11)	34 (4)
C(28′)	0·2651 (7)	0·0932 (13)	−0·0511 (14)	64 (6)
C(27′)	0·1902 (7)	0·0707 (12)	0·4417 (14)	63 (6)

Table 2. *Geometrical characteristics of the complex*

(a) Bond distances (Å) with the corresponding e.s.d.'s in parentheses

X =	−	1	2
N(X1)−N(X2)	1·353 (14)	1·356 (15)	1·363 (14)
N(X1)−C(X5)	1·360 (12)	1·361 (14)	1·327 (17)
N(X2)−C(X3)	1·329 (12)	1·368 (13)	1·374 (13)
C(X3)−C(X4)	1·411 (15)	1·381 (18)	1·369 (18)
C(X3)−C(X7)	1·489 (18)	1·460 (19)	1·495 (16)
C(X4)−C(X5)	1·401 (16)	1·376 (15)	1·395 (14)
C(X4)−C(X6)	1·504 (13)	1·528 (14)	1·482 (16)
C(X5)−C(X8)	1·472 (18)	1·509 (20)	1·518 (22)
C(X6)−C(X4′)	1·522 (18)	1·537 (17)	1·504 (18)
N(X1′)−N(X2′)	1·388 (15)	1·347 (15)	1·390 (14)
N(X2′)−C(X3′)	1·322 (16)	1·366 (17)	1·372 (15)
N(X1′)−C(X5′)	1·332 (15)	1·323 (16)	1·336 (16)
C(X5′)−C(X4′)	1·405 (19)	1·415 (17)	1·392 (16)
C(X5′)−C(X8′)	1·515 (21)	1·495 (18)	1·472 (19)
C(X4′)−C(X3′)	1·366 (16)	1·389 (16)	1·381 (17)
C(X3′)−C(X7′)	1·508 (21)	1·482 (20)	1·479 (18)

Table 2 *(cont.)*

Co(1)−Cl(1)	2·253 (3)	Co(3)−Cl(21)	2·254 (5)
Cl(2)	2·228 (4)	Cl(22)	2·230 (4)
N(1)	2·008 (8)	N(21)	2·012 (9)
N(21′)	2·026 (10)	N(1′)	2·006 (11)
Co(2)−Cl(11)	2·239 (4)	C(31)−C(32)	1·36 (9)
Cl(12)	2·234 (4)	C(31)−O	1·25 (6)
N(11)	1·992 (8)		
N(11′ⁱᵛ)	2·028 (11)		

(b) Bond angles (°) with e.s.d.'s in parentheses

X =	−	1	2
C(X5)−N(X1)−N(X2)	104·8 (8)	104·8 (8)	105·8 (9)
N(X1)−N(X2)−C(X3)	113·3 (8)	112·1 (10)	110·2 (10)
N(X2)−C(X3)−C(X4)	106·5 (10)	105·5 (11)	107·1 (9)
−C(X7)	123·1 (9)	121·1 (11)	121·5 (12)
C(X4)−C(X3)−C(X7)	130·3 (9)	133·4 (10)	131·5 (10)
C(X3)−C(X4)−C(X5)	104·9 (8)	107·2 (9)	105·5 (10)
−C(X6)	127·3 (10)	125·8 (10)	127·4 (10)
C(X5)−C(X4)−C(X6)	127·8 (10)	127·0 (11)	127·0 (12)
C(X4)−C(X5)−N(X1)	110·4 (10)	110·4 (11)	111·3 (12)
−C(X8)	129·5 (9)	131·9 (10)	127·2 (12)
N(X1)−C(X5)−C(X8)	120·1 (9)	117·7 (9)	121·5 (10)
C(X4)−C(X6)−C(X4′)	112·4 (10)	114·7 (8)	117·1 (10)
C(X3′)−N(X2′)−N(X1′)	110·5 (9)	112·1 (9)	110·4 (10)
N(X2′)−N(X1′)−C(X5′)	105·6 (10)	106·6 (10)	105·3 (9)
N(X1′)−C(X5′)−C(X4′)	109·8 (11)	109·9 (10)	111·2 (11)
−C(X8′)	120·8 (12)	121·6 (11)	117·9 (11)
C(X4′)−C(X5′)−C(X8′)	129·4 (11)	128·5 (11)	130·9 (12)
C(X5′)−C(X4′)−C(X3′)	105·7 (11)	106·0 (10)	106·5 (11)
−C(X6)	127·8 (11)	128·0 (11)	129·6 (11)
C(X3′)−C(X4′)−C(X6)	126·5 (12)	125·9 (11)	123·9 (11)
C(X4′)−C(X3′)−N(X2′)	108·4 (11)	105·3 (11)	106·6 (10)
−C(X7′)	131·4 (12)	130·9 (12)	132·0 (12)
N(X2′)−C(X3′)−C(X7′)	120·1 (10)	123·8 (11)	121·4 (11)

Cl(1)−Co(1)−Cl(2)	115·7 (1)	Cl(21)−Co(3)−Cl(22)	115·3 (2)
−N(1)	100·4 (3)	−N(1′)	113·4 (4)
−N(21′)	115·2 (3)	−N(21)	103·0 (4)
Cl(2)−Co(1)−N(1)	116·0 (3)	Cl(22)−Co(3)−N(1′)	103·3 (3)
−N(21′)	104·3 (3)	−N(21)	115·5 (3)
N(1)−Co(1)−N(21′)	105·2 (3)	N(1′)−Co(3)−N(21)	106·4 (4)
Cl(11)−Co(2)−Cl(12)	122·8 (2)	C(32)−C(31)−O	116 (6)
−N(11)	103·4 (3)		
−N(11′ⁱᵛ)	112·0 (3)		
Cl(12)−Co(2)−N(11)	111·3 (3)		
−N(11′ⁱᵛ)	101·4 (3)		
N(11)−Co(2)−N(11′ⁱᵛ)	104·8 (4)		

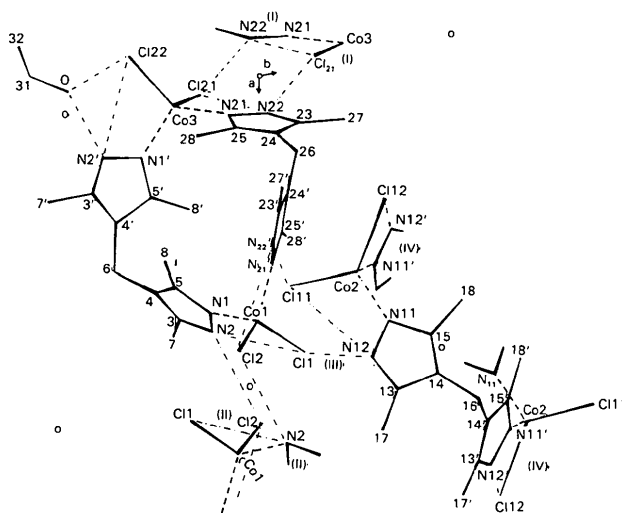Symmetry code: (iv) $1-x$, $1-y$, $1-z$.

Fig. 1. The crystal structure of the title compound viewed down the c axis, showing the atomic numbering and the hydrogen-interactions network. (For the symmetry code relating the interacting atoms see Table 3.)

The Co atom is tetrahedrally linked to two Cl atoms and to two N atoms. In terms of the external consistency of the weighted means (Topping, 1960, and references therein), the Co—Cl bond lengths are just significantly lower (Laing & Carr, 1975) than in tetrahedral $CoCl_4$ groups (Bkouche-Waksman & L'Haridon, 1977; Blake Vance, Holt, Pierpont & Holt, 1980). The Co—N distances have values intermediate between those assigned to tetrahedral and those to octahedral coordination (Reedijk, Jansen, van Koningsveld & van Kralingen, 1978). The coordinating angles show deformations from the tetrahedral value of approximately similar type in the three tetrahedra, involving an enlargement of the Cl—Co—Cl angle [115·3 (2)–122·8 (2)°], a narrowing of the N—Co—N angle [104·8 (4)–106·4 (4)°] and a 'concerted' enlargement/narrowing of the Cl—Co—N angles [111·3 (3)–116·0 (3)°]/[100·4 (3)–104·3 (3)°], as shown in Fig. 2.

Within the achieved accuracy, the geometry of the five-membered rings is quite constant along the six crystallographically independent rings. In each ring the endocyclic angles at the N atom not coordinating to metal and that at the C atom adjacent to the N atom involved in coordination are systematically higher (110–113°) than the other endocyclic angles (105–108°), as happens in other Co—pyrazole complexes (Churchill, Gold & Maw, 1970; Guggenberger, Prewitt, Meakin, Trofimenko & Jesson, 1978; Reedijk et al., 1978), while it seems that this effect does not occur in uncoordinated pyrazoles (Gieren & Pertlik, 1975). The C—methyl distances and the C—C(X) lengths ($X = 6$, 16, 26) are not significantly different. The C(X) substituents are symmetrically bound to the rings, as estimated from the C—C—C(X) angles which are equal, while, although the types of bond are not the same, the other substituents are not symmetrically bound, having Co—N—N < Co—N—C and N—C—Me < C—C—Me.

The location of the ethanol-molecule atoms is imprecise and their thermal factors so high that the observed shortening in lengths (Bkouche-Waksman & L'Haridon, 1977) lacks any meaning.

Both dimers can be described through the torsion angles in the two macrorings (see Fig. 3), the pyrazole rings being planar within the limits of achieved accuracy. These macrorings differ considerably: while the one through Co(3)···N(21)···Co(1)··· has local

$\overline{4}2m$ approximate symmetry, with sequence of torsion angles: $[-g^--a]$ $-a-g^+-g^+-a-a-g^--g^--a-a-g^+-g^+-a-a-g^--$, the macroring through Co(2^{iv})··· N(11')···Co(2)··· has almost $2/m$ symmetry where the sequence is $[-g^--a-a-(ga)^+]$ $-(ga)^--a-a-g^+-g^+-a-a-(ga)^--(ga)^+-a-a-g^--$. Within brackets are the pseudo-independent parts; $g^\pm$ stands for angles in the range ±75°, a for the range 180 ± 30° (Urbańczyk-Lipkowska, Krajewski, Gluziński, Andreetti & Bocelli, 1981) and $(ga)^\pm$ for the range ±75–150°. In the first macroring the weighted average and the external consistency (Topping, 1960, and references therein) of the g-type angles, in absolute value, is 50·9 (29)° and for the a type is 175·0 (15)°. In the other macroring these averages are 44·7 (10) and 172·5 (28)° and there is another type, situated around C(16) and C(16^{iv}), the (ga) one with an average of 88·7 (31)°. This conformation places the pyrazole rings, say, in the first macroring alternately up and down with respect to each other while in the second macroring there are two pyrazole rings both up, followed by two down (see Fig. 3).

Angles between different portions of the complex in both dimers with respect to the least-squares planes defined by Co(1)···C(6)···Co(3)···C(26) and Co(2)··· C(16)···Co(2^{iv})···C(16^{iv}) are given in a deposited table,

Fig. 3. The two dimers present in the structure as viewed down the axis perpendicular to the best least-squares planes through Co(1)···C(6)···Co(3)···C(26) and Co(2)···C(16)···Co(2^{iv})··· C(16^{iv}) respectively. Deviations from the first plane are 0·275 (2) Å for Co(1) and Co(3), and −0·275 (12) Å for C(6) and C(26). The other set is planar.
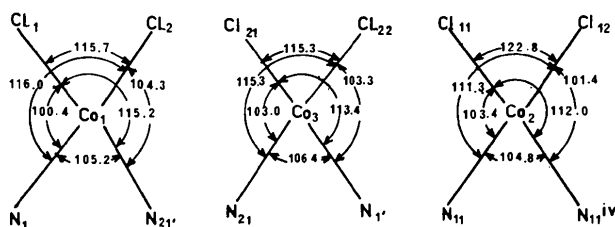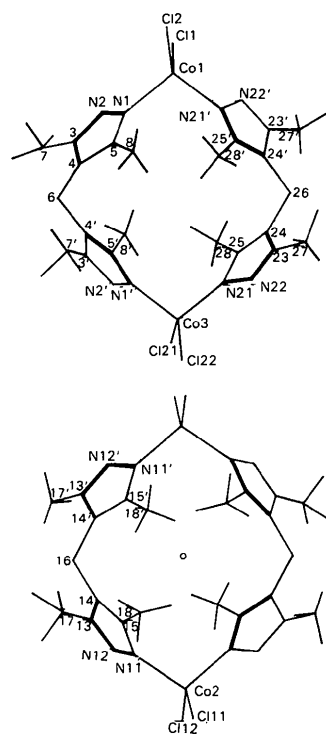

Fig. 2. Coordination angles (°) around the Co atom. E.s.d.'s are in the ranges: Cl—Co—Cl 0·1–0·2, Cl—Co—N 0·3–0·4, N—Co—N 0·3–0·4°.

$$C_{22}H_{32}Cl_4Co_2N_8.\tfrac{2}{3}C_2H_6O$$

with corresponding values between both macrorings quite similar, although the first reference plane, Co(1)–C(26), is not planar.

The hydrogen interactions (see Fig. 1) are shown in Table 3, where those contacts more likely to be hydrogen bonds are marked with an asterisk (Schuster, Zundel & Sandorfy, 1976; Whuler, Brouty & Spinat, 1980). Note that the H atom attached to the ethanol oxygen could not be located. Within the dimers we may notice some short contacts between H atoms of the methyl substituents (see Fig. 3), namely, in Å, H(8a) ···H(28a) = 2·3 (2), H(8'c)···H(28'b) = 2·5 (2), H(17'c)···H(18a) = 2·4 (2), H(17'c)···H(18c) = 2·6 (2), H(17'a)···H(18c) = 2·8 (2), H(17a)··· H(18'c) = 2·5 (3) and H(17c)···H(18'c) = 2·4 (3). When we consider the hydrogen positions in the same directions but at 1·08 Å from the bonded C (Passer, White, Goldman & Lerit, 1980), those values become, in the same sequence, 2·1, 2·3, 2·3, 2·6, 2·8, 2·1 and 2·1 Å.

Table 3. *Main hydrogen interactions*

Distances are in Å and angles in °, followed by the e.s.d.'s in parentheses.

X–H···Y	X···Y	H···Y	X–H···Y
N(2')–H(2')···O*	3·039 (56)	2·23 (11)	142 (8)*
N(2')–H(2')···Cl(22')	3·395 (11)	2·70 (10)	130 (8)*
N(22')–H(22')···Cl(11')	3·316 (10)	2·30 (11)	156 (9)*
N(22')–H(22')···Cl(2')	3·445 (11)	3·06 (12)	101 (7)
N(2)–H(2)···Cl(2ⁱⁱ)	3·624 (9)	2·79 (12)	156 (10)*
N(2)–H(2)···Cl(1')	3·331 (8)	2·81 (11)	118 (9)
N(12)–H(12)···Cl(1ⁱⁱⁱ)	3·362 (11)	2·58 (16)	142 (11)*
N(12)–H(12)···Cl(11')	3·413 (8)	3·03 (13)	106 (10)
N(12')–H(12')···Cl(12ⁱᵛ)	3·423 (11)	2·83 (11)	116 (7)
N(22)–H(22)···Cl(21ⁱ)	3·320 (12)	2·49 (16)	127 (9)
N(22)–H(22)···Cl(21')	3·410 (16)	2·58 (12)	127 (10)
O···Cl(22')	3·302 (67)	–	–

Symmetry code: (i) $-x, -y, -1-z$; (ii) $1-x, -y, -z$; (iii) $x, y, 1+z$; (iv) $1-x, 1-y, 1-z$; (v) x, y, z.

* Contacts more likely to be hydrogen bonds.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A27, 157–165.
BKOUCHE-WAKSMAN, I. & L'HARIDON, P. (1977). *Acta Cryst.* B33, 11–21.
BLAKE VANCE, T., HOLT, E. M., PIERPONT, C. G. & HOLT, S. L. (1980). *Acta Cryst.* B36, 150–153.
CHURCHILL, M. R., GOLD, K. & MAW, C. E. (1970). *Inorg. Chem.* 9(7), 1597–1604.
CUADRO, A., ELGUERO, J. & NAVARRO, P. (1981). VIII Int. Congr. Heterocycl. Chem. Graz, Austria.
GIEREN, V. A. & PERTLIK, F. (1975). *Acta Cryst.* B31, 2431–2440.
GUGGENBERGER, L. J., PREWITT, C. T., MEAKIN, P., TROFIMENKO, S. & JESSON, J. P. (1973). *Inorg. Chem.* 12(3), 508–515.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LAING, M. & CARR, G. (1975). *Acta Cryst.* B31, 2683–2684.
MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS.* Instituto 'Rocasolano', CSIC, Madrid.
NARDELLI, M. (1982). *PARST. A System of Fortran Routines for Calculating Molecular Structure Parameters from Results of Crystal Structure Analysis.* Univ. of Parma, Italy.
PASSER, E. L., WHITE, J. G., GOLDMAN, N. L. & LERIT, A. H. (1980). *Acta Cryst.* B36, 1856–1860.
REEDIJK, J., JANSEN, J. C., VAN KONINGSVELD, H. & VAN KRALINGEN, C. G. (1978). *Inorg. Chem.* 17(7), 1990–1994.
ROGER, E., SANTOS, A., CUADRO, A., ELGUERO, J. & NAVARRO, P. (1982). *An. Quím. Ser. A.* In the press.
SCHUSTER, P., ZUNDEL, G. & SANDORFY, C. (1976). *The Hydrogen Bond.* Vol. II. Amsterdam: North-Holland.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
TOPPING, J. (1960). *Errors of Observation and Their Treatment,* pp. 91–115. London: Chapman & Hall.
URBAŃCZYK-LIPKOWSKA, Z., KRAJEWSKI, J. W., GLUZIŃSKI, P., ANDREETTI, G. D. & BOCELLI, G. (1981). *Acta Cryst.* B37, 470–473.
USON, R., ORO, L. A., ESTEBAN, M., CUADRO, A., ELGUERO, J. & NAVARRO, P. (1982). *Transition Met. Chem.* To be published.
WHULER, A., BROUTY, C. & SPINAT, P. (1980). *Acta Cryst.* B36, 1267–1269.