Crystal and Molecular Structure of Chloro[*NN'*-di-(3-aminopropyl)-piperazine]nickel(II) Chloride

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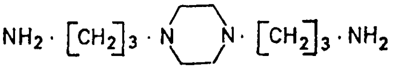
The structure of the title compound has been determined by a three-dimensional *X*-ray structural analysis, by use of 1967 independent reflections obtained photographically. Crystals are monoclinic with $a = 7{\cdot}85(3)$, $b = 14{\cdot}47(3)$, $c = 14{\cdot}14(3)$, $\beta = 110{\cdot}00(5)°$, space group $P2_1/c$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods to *R* 0·084. The cation is five-co-ordinate with a geometry approximating to a square pyramid. The four nitrogens of the tetra-amine are closely co-planar, with the nickel 0·34 Å out of this plane towards the covalently bound chlorine [Ni–N(primary) 2·103(7) and 2·107(7); Ni–N(tertiary) 2·052(8) and 2·053(8); Ni–Cl 2·338(3) Å]. The N_4 plane, however, is distorted from a square by ligand constraints, so that N–Ni–N angles (between adjacent nitrogens) are 72·0(3)—95·2(3)°. Bond lengths within the cation have normal covalent values; the chloride ion forms a specific hydrogen-bonded ion-pair with the cation so as to be near the (sterically hindered) 'sixth co-ordination site' of the nickel [Ni–Cl 3·395(3) Å]. The analysis shows the steric over-crowding of the ligand system (B-strain) which accounts for the low stability constants of its metal compounds.

As part of a general interest in the relationship between ligand steric effects and metal stereochemistry, we have investigated recently[1,2] some transition-metal compounds of the linear tetra-amine (I). The steric effects


(I)

(*B*-strain)[3] which lead to the formation of five-co-ordinate compounds [MLX]Y [where L = (I); M = Co, Ni, or Cu; X and Y are unit-charge anions] have been discussed already,[1,2] and we have given a preliminary report[1] of an *X*-ray investigation of the structure of [NiLCl]Cl, a key compound in the series. We now give details of the final refinement of the structure.

EXPERIMENTAL

Blue-green prisms were obtained from *NN'*-dimethylformamide.[2] The data crystal (0·2 × 0·25 × 0·3 mm) was mounted in a thin-walled Lindeman glass capillary. Unit-cell dimensions were measured from precession photographs (Zr-filtered Mo-K_α radiation).

Crystal Data.—$C_{10}H_{24}Cl_2N_4Ni$, $M = 329{\cdot}9$, Monoclinic, $a = 7{\cdot}85(3)$, $b = 14{\cdot}47(3)$, $c = 14{\cdot}14(3)$ Å, $\beta = 110{\cdot}00(5)°$, $U = 1596$ Å^3, $D_m = 1{\cdot}46$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1{\cdot}49$ g cm^{-3}, $F(000) = 696$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 46{\cdot}32$ cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences.

Layers {0—7*kl*} were collected photographically by the equi-inclination Weissenberg method, and intensities were estimated visually. The usual Lorentz, polarization, and spot-shape corrections were applied. No corrections were made for absorption. The final data set consisted of 1967 independent observed reflections obtained from the Cu-K_α data.

The data set used for the initial refinement[1] of the structure consisted of 0—4*kl* Cu-K_α Weissenberg layers, together with *h*0*l*—*h*3*l* and *hk*0 Mo-K_α precession data. The positions of the nickel and of one of the chlorine atoms were established from a Patterson synthesis, and a Fourier synthesis then gave the positions of all other non-hydrogen atoms. Successive cycles of block-diagonal least-squares refinement reduced *R*, to 0·12 with isotropic thermal parameters, and to 0·096, with both anisotropic thermal parameters and the inclusion of hydrogen atoms at calculated positions. (All of the latter were clearly defined on a difference Fourier map.)

This refined structure was then used to calculate inter-layer scales for the complete Cu-K_α Weissenberg data set (the Mo-K_α data now being eliminated). Anomalous dispersion corrections (both $\Delta f'$ and $\Delta f''$)[4] were applied for both the nickel and the chlorine atoms, and a non-unit weighting scheme was introduced: $w = 1/\{1 + [(|F_o| - 36)/50]^2\}$. The final refinement proceeded as follows: all non-hydrogen atoms with anisotropic *B* factors, *R* 0·097; inclusion but non-refinement of hydrogens [calculated assuming C–H 1·00, and N–H 0·96 Å and given isotropic *B* factors 2·0 (C–H) or 1·0 (N–H) greater than the final refined values for the atoms to which they are attached], final *R* 0·084.

Atomic scattering factors for neutral non-hydrogen atoms were taken from ref. 5, and for hydrogen from ref. 6. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20958 (22 pp., 1 microfiche).†

Programmes used were part of the Sheffield *X*-ray system; calculations were performed on the Chilton Atlas and Sheffield University ICL 1907 computers.

Final atomic positions and thermal parameters, together with the estimated standard deviations, are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

The structure analysis confirms the initial assignment of a five-co-ordinate geometry for the nickel(II) species (Figure 1). Details of the various bond lengths and angles are in Table 3, and relevant equations of least-squares planes and inter planar angles are in Table 4.

The nickel(II) cation has a structure approximating to a square pyramid (Figure 1, Table 3). The four donor

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[1] N. A. Bailey, J. G. Gibson, and E. D. McKenzie, *Chem. Comm.*, 1969, 741.

[2] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1029.

[3] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.

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[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 1

Atomic positions $(\times 10^4)$, with estimated standard deviations in parentheses, and calculated hydrogen positions $(\times 10^3)$, with the isotropic thermal parameters which were used in the final refinement

Atom	x/a	y/b	z/c	B
Ni	1687(2)	1035(1)	1620(1)	
Cl(1)	−0396(3)	−0159(2)	1468(2)	
Cl(2)	4286(3)	2602(2)	0950(2)	
N(1)	0304(9)	1714(5)	0307(5)	
N(2)	0882(9)	1944(5)	2549(5)	
N(3)	3465(10)	0853(5)	3109(5)	
N(4)	3330(10)	0388(5)	0964(6)	
C(1)	8674(12)	2227(7)	0259(7)	
C(2)	9068(14)	2954(7)	1109(9)	
C(3)	9264(14)	2530(8)	2126(9)	
C(4)	2571(12)	2488(7)	2983(7)	
C(5)	4185(12)	1826(6)	3335(7)	
C(6)	0710(14)	1352(8)	3390(8)	
C(7)	2311(15)	0684(8)	3715(7)	
C(8)	4937(15)	0164(8)	3341(9)	
C(9)	5807(13)	0077(8)	2560(8)	
C(10)	4613(14)	−0328(7)	1570(8)	
H(1) *	−225	178	032	4·9
H(1′)	−181	255	−041	4·9
H(2)	−196	341	093	6·1
H(2′)	022	328	116	6·1
H(3)	−184	214	204	6·1
H(3′)	−067	304	261	6·1
H(4)	251	286	357	5·1
H(4′)	272	291	246	5·1
H(5)	483	190	407	4·9
H(5′)	504	196	297	4·9
H(6)	−045	100	314	5·6
H(6′)	073	175	397	5·6
H(7)	185	003	361	5·8
H(7′)	302	078	444	5·8
H(8)	442	−045	342	6·1
H(8′)	589	034	399	6·1
H(9)	690	−033	284	6·1
H(9′)	620	071	243	6·1
H(10)	391	−086	170	5·8
H(10′)	539	−055	118	5·8
H(11)[N(1)]	−004	127	−022	3·6
H(12)[N(1)]	113	215	018	3·6
H(13)[N(4)]	256	010	036	3·7
H(14)[N(4)]	403	086	079	3·7

* Hydrogen attached to carbon is numbered according to that carbon atom, pairs on the same carbon being distinguished by primes. Where hydrogen is attached to nitrogen, the number of the corresponding nitrogen atom is given in square brackets.

TABLE 2

Anisotropic thermal vibrational parameters * $(\times 10^5)$, with estimated standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ni	1132(4)	236(1)	266(1)	−66(2)	185(3)	81(3)
Cl(1)	1899(8)	350(2)	416(2)	−169(3)	599(6)	−558(6)
Cl(2)	1770(8)	543(2)	548(3)	140(4)	450(7)	−277(7)
N(1)	1252(24)	307(6)	404(7)	46(11)	194(19)	177(18)
N(2)	1261(23)	346(6)	326(7)	−275(10)	292(18)	−239(18)
N(3)	1592(24)	306(6)	254(7)	34(10)	240(18)	−48(18)
N(4)	1323(25)	347(7)	418(8)	190(11)	406(20)	192(19)
C(1)	1139(29)	402(8)	534(10)	15(15)	137(25)	327(23)
C(2)	1998(38)	284(8)	821(14)	−107(16)	529(34)	450(27)
C(3)	1866(36)	470(10)	747(13)	−620(19)	731(33)	235(29)
C(4)	1468(31)	354(8)	505(10)	−244(14)	480(26)	−463(24)
C(5)	1498(30)	341(8)	355(9)	−133(13)	56(23)	−410(23)
C(6)	2143(39)	564(11)	449(10)	−298(16)	1043(30)	−809(30)
C(7)	2356(40)	505(10)	395(10)	−45(15)	603(29)	−979(31)
C(8)	2152(39)	455(10)	507(11)	147(16)	−56(30)	619(29)
C(9)	1364(32)	525(10)	674(12)	42(18)	190(29)	551(28)
C(10)	1776(35)	415(9)	620(11)	−88(16)	669(30)	746(28)

* The expression for the temperature factors is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

nitrogens are closely co-planar (Table 4) in a quadrilateral which is markedly distorted from the square by the constraints of the ligand structure. Angles at the

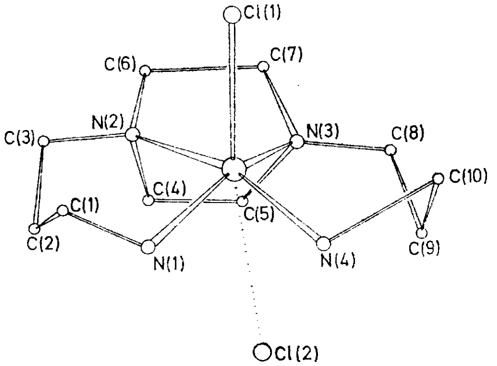

FIGURE 1 Molecular geometry and atom labelling scheme

TABLE 3

Interatomic distances and angles with estimated standard deviations in parentheses

(*a*) The co-ordination sphere of the metal

(i) Bond lengths (Å)

Ni–Cl(1)	2·338(3)	Ni–N(3)	2·107(7)
Ni–N(1)	2·052(8)	Ni–N(4)	2·053(8)
Ni–N(2)	2·103(7)		

(ii) Bond angles (°)

Cl(1)–Ni–N(1)	97·7(2)	N(1)–Ni–N(3)	158·2(3)
Cl(1)–Ni–N(2)	99·8(2)	N(1)–Ni–N(4)	91·7(3)
Cl(1)–Ni–N(3)	101·7(2)	N(2)–Ni–N(3)	72·0(3)
Cl(1)–Ni–N(4)	98·6(2)	N(2)–Ni–N(4)	159·5(3)
N(1)–Ni–N(2)	95·0(3)	N(3)–Ni–N(4)	95·2(3)

(*b*) The tetra-amine ligand

(i) Bond lengths (Å)

N(1)–C(1)	1·46(1)	N(2)–C(6)	1·51(1)
C(1)–C(2)	1·55(1)	C(6)–C(7)	1·53(2)
C(2)–C(3)	1·52(2)	C(7)–N(3)	1·46(1)
C(3)–N(2)	1·47(1)	N(3)–C(8)	1·48(1)
N(2)–C(4)	1·48(1)	C(8)–C(9)	1·49(2)
C(4)–C(5)	1·53(1)	C(9)–C(10)	1·51(2)
C(5)–N(3)	1·51(1)	C(10)–N(4)	1·49(1)

(ii) Bond angles (°)

Ni–N(1)–C(1)	118·0(6)	Ni–N(4)–C(10)	117·4(6)
N(1)–C(1)–C(2)	111·8(8)	N(4)–C(10)–C(9)	110·3(9)
C(1)–C(2)–C(3)	112·9(9)	C(10)–C(9)–C(8)	115·0(9)
C(1)–C(3)–N(2)	114·2(9)	C(9)–C(8)–N(3)	114·5(9)
C(3)–N(2)–Ni	120·5(6)	C(8)–N(3)–Ni	120·5(6)
C(3)–N(2)–C(4)	112·8(8)	C(8)–N(3)–C(5)	112·0(7)
C(3)–N(2)–C(6)	110·4(8)	C(8)–N(2)–C(7)	110·6(8)
Ni–N(2)–C(4)	100·0(5)	Ni–N(3)–C(5)	99·7(5)
Ni–N(2)–C(6)	105·4(6)	Ni–N(3)–C(7)	105·9(6)
C(4)–N(2)–C(6)	106·5(7)	C(5)–N(3)–C(7)	107·0(7)
N(2)–C(4)–C(5)	109·1(8)	N(3)–C(5)–C(4)	107·8(7)
N(2)–C(6)–C(7)	108·1(8)	N(3)–C(7)–C(6)	109·2(9)

(*c*) Hydrogen bonding

(i) Interatomic distances (Å)

Cl(2) · · · N(1)	3·210(8)	Cl(1) · · · N(1^{I})	3·389(8)
Cl(2) · · · N(4)	3·291(8)	Cl(1) · · · N(4^{I})	3·438(8)

(ii) Interatomic angles (°)

Cl(2) · · · H(12) · · · N(1)	137·9(5)
Cl(2) · · · H(14) · · · N(4)	135·9(5)
Cl(1) · · · H(11) · · · N(1^{I})	156·5(5)
Cl(1) · · · H(13) · · · N(4^{I})	151·7(5)

Atoms with superscript I are at $-x, -y, -z$.

nickel vary between 95·2(3) and 72·0(3)°, the smaller angle referring to the piperazine chelate ring and the larger to the trimethylene chelate rings (Table 3). The four sides of the N_4 quadrilateral are (in cyclic order) 2·48(1), 3·07(1), 2·95(1), and 3·06(1) Å.

The Ni–N distances have normal covalent values, the bonds to the tertiary being significantly longer than those to the primary ones (Table 3). The metal atom is 0·34 Å out of the N_4 plane in the direction of the covalently bound chlorine. The N · · · Cl vector is nearly perpendicular to the N_4 plane and the bond length of 2·338(3) Å is also a normal covalent one, being intermediate between those for octahedral[7] and tetrahedral[8] nickel(II) species. The covalent radius of nickel (1·35 Å) derived from the present Ni–N bond lengths predicts the value found for the Ni–Cl bond length.

TABLE 4

Equations to the least-squares planes, in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c^*). Deviations (Å) of various atoms from the planes are given in square brackets

	l	m	n	d
Plane (1)				
N(1)—(4)	0·6640	0·7461	0·0493	1·9192
[Ni −0·34, N(1) 0·01, N(2) −0·01, N(3) 0·01, N(4) −0·01]				
Plane (2)				
C(4)—(7)	−0·0654	0·3609	0·9303	4·9575
[C(4) −0·01, C(5) 0·01, C(6) 0·01, C(7) −0·01]				
Plane (3)				
N(2), C(4), C(6)	0·6404	−0·7273	−0·2468	−3·2274
Plane (4)				
N(3), C(5), C(7)	0·5708	−0·3442	0·7454	3·3487
Plane (5)				
N(1), N(2), C(1), C(3)	0·5660	0·8244	−0·0020	2·0498
[Ni −0·51, N(1) 0·05, N(2) −0·04, C(1) −0·05, C(3) 0·05, C(2) 0·75]				
Plane (6)				
C(1)—(3)	−0·9747	0·1129	−0·1930	1·4336
Plane (7)				
N(1), N(2), Ni	−0·8157	−0·5681	−0·1093	−1·5270
Plane (8)				
N(3), N(4), C(8), C(10)	−0·7434	−0·6672	−0·0462	−1·9750
[Ni 0·47, N(3) 0·06, N(4) −0·06, C(8) −0·07, C(10) 0·07, C(9) −0·73]				
Plane (9)				
C(8)—(10)	−0·2166	0·9178	−0·3328	−1·7492
Plane (10)				
N(3), N(4), Ni	0·4827	0·8744	−0·0487	1·4655

Angles (°) between planes

(1)—(2)	74·2	(5)—(6)	117·3
(2)—(3)	122·3	(5)—(7)	158·4
(2)—(4)	57·9	(8)—(9)	115·8
	(122·1)	(8)—(10)	160·1

The ' sixth co-ordination site ' of the metal is blocked by the piperazine moiety, the C_4 plane of which is at an angle of 74·2° to the N_4 co-ordination plane (Table 4). The non-co-ordinated chloride is ' displaced ' from this site [Ni · · · Cl(2) 3·395(3) Å] and sits over the primary amine groups to which it is hydrogen bonded (Table 3 and Figure 2). Such ion-pairs persist in non-aqueous solutions of this and related compounds.[2] Here, the units are held together in pairs (Figure 3) by hydrogen bonding between the covalently bound chlorine and the primary nitrogens of an adjacent molecule. Thus, all four hydrogens of the primary amines are involved in hydrogen bonding (Table 3 and Figure 3).

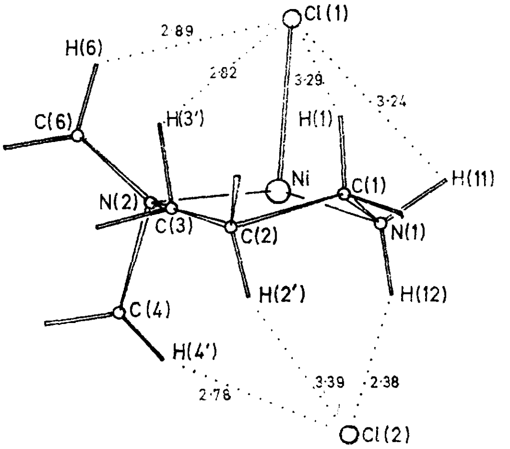

FIGURE 2 A side-on projection showing one-half of the molecule and the close intramolecular contacts of the two chlorine atoms

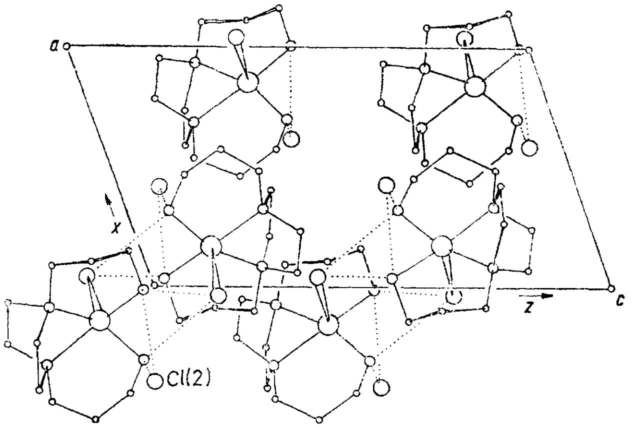

FIGURE 3 The arrangement of the atoms in the unit cell, showing how pairs of molecular ions are held together by the hydrogen bonding (represented by dotted lines). The boundary line is drawn at $z = \frac{1}{2}$

Angles and bond lengths in the tetra-amine ligand are generally as expected and compare favourably, for example, with those found[9] in 1,4-piperazine-γ,γ'-dibutyric acid. The piperazine ring is held in the unstable boat conformation, but the trimethylene chelate

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TABLE 5

Hydrogen–hydrogen contacts $<2{\cdot}4$ Å[a]

(*a*) Intramolecular contacts (Å)[b,c]

H(1) ··· H(3)	2·38	H(5′) ··· H(9′)	2·19
H(1) ··· H(11)	2·33	H(5) ··· H(7′)	2·32
H(1′) ··· H(2)	2·37	H(6′) ··· H(7′)	2·26
H(1′) ··· H(12)	2·32	H(6) ··· H(7)	2·26
H(1′) ··· H(11)	2·36	H(7) ··· H(8)	2·22
H(2′) ··· H(4′)	2·16	H(8′) ··· H(9)	2·34
H(2) ··· H(3′)	2·39	H(8) ··· H(10)	2·38
H(3) ··· H(6)	2·27	H(9′) ··· H(14)	2·36
H(4′) ··· H(5′)	2·26	H(9) ··· H(10′)	2·32
H(4) ··· H(5)	2·26	H(10′) ··· H(14)	2·35
H(4) ··· H(6′)	2·31	H(10 ··· H(13)	2·37

(*b*) Intermolecular contacts (Å)

H(2) ··· H(7$^{\mathrm{II}}$)	2·30	H(6′) ··· H(12$^{\mathrm{IV}}$)	2·14
H(6) ··· H(9$^{\mathrm{III}}$)	2·39		

[a] These values were calculated not with the hydrogen positions of Table 1, but with new positions assuming more real internuclear distances of C–H 1·09, and N–H 1·04 Å. [b] Those between pairs of methylene and NH_2 hydrogen atoms have been omitted. [c] Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

II $-x, \frac{1}{2}+y, \frac{1}{2}-z$ IV $x-1, y, z$
III $x, \frac{1}{2}-y, \frac{1}{2}+z$

rings have distorted chair conformations (both ring types are defined by three interplanar angles, Table 4). The latter are flattened and somewhat twisted [planes (5) and (8), Table 4] at least partially as a result of ligand constraints in this molecule, and associated with this are larger-than-normal angles of 95° at the nickel; the N–C–C and C–C–C bond angles in these chelate rings are also significantly greater than the ideal tetrahedral values (Table 3).

As well as this bond-angle strain, there are a significant number of H ··· H contacts $<2{\cdot}4$ Å (Table 5), which imply a somewhat overcrowded structure. These effects are undoubtedly an important cause of the low stability constants of the metal compounds of this ligand.[10] (The value of 2·4 Å as the assumed van der Waal's separation of two hydrogen atoms is arbitrary and has no absolute meaning. Hydrogen atoms are relatively ' soft ' and can approach significantly closer than this. However, there are here a large number of intramolecular distances less than this value, but very few intermolecular ones.)

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[3/2257 *Received, 2nd November*, 1973]

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