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The Crystal and Molecular Structure of *Cis*-Chlorobis(Ethylenediamine)-Imidazole Cobalt(III) Chloride, $[Co(en)_2(Im)Cl]Cl_2$

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The crystal structure of cis-*chlorobis(ethylenediamine)imidazole cobalt(III) chloride,* $[Co(en)_2(Im)Cl]Cl_2$, *has been determined by X-ray methods. The compound crystallises in a monoclinic system of space group* $P2_1/c$, *with* a = *830.3(4),* b = *1352(1),* c = *1516.9(7) pm,* β = *124.75(3),* V = *1399* × 10^6 pm^3, Z = *4,* D*(calc) = 1.68 g* cm^{-3}. *The coordination around the cobalt(III) centre is octahedral and the bond distances are Co–N(en) (average) 196.0(7) pm; Co–N (Im) 194.5(7) pm and Co–Cl 225.7(3) pm. One of the two coordinated ethylenediamine ligands is bonded in an equatorial–axial manner, while the other one is bonded in the equatorial–equatorial way. The imidazole ring is planar within the standard deviations.*

Introduction

We have been interested in investigating the coordinating abilities of the biologically important ligand imidazole and its derivatives [1–6], which are known to serve as simple 'model' compounds. The transition metal complexes involving mixed ligand systems are of physiological significance. Most of the available information on mixed ligand complexes of imidazole with transition metal ions are concerned with studies in solution [7]. As a part of our studies on mixed ligand complexes of transition metals involving imidazole ligands [5, 6, 8–11], we have recently reported [11] complexes of the type $[Co(en)_2(L)Cl]Cl_2$ (where L = imidazole or its substituted derivatives) obtained by the reaction of *trans*-$[Co(en)_2Cl_2]Cl$ with the imidazole ligands. These were shown to have a *cis*-structure on the basis of i.r. and n.m.r. (^1H and ^{13}C) studies. The proposed *cis*-structure of the complexes [11] has now been established by an X-ray crystal structure analysis of $[Co(en)_2(Im)Cl]Cl_2$ complex. The compound $[Co(en)_2(NCS)_2]Cl$, prepared similarly from *trans*-$[Co(en)_2Cl_2]Cl$ and KCNS, already has been shown to have a *cis*-structure [12]. The analogous mixed ligand complex $[Co(acac)_2(Im)(NO_2)]$, has a *trans*-configuration [10], however.

Experimental

Preparation of the Crystals

The title compound was synthesised as described earlier [11]. Slow evaporation of the aqueous solution of the compound at room temperature yielded brick-red crystals of *cis*-$[Co(en)_2(Im)Cl]Cl_2$.

Crystal Data and Intensity Measurements

The lattice parameters were determined by precession photographs. Refinement of these parameters and intensity measurements were performed on a four circle automatic diffractometer Syntex $P2_1$ using Mo-K_α radiation (graphite monochromator, λ = 71.069 pm). Crystal data are: $CoC_7H_{20}N_6Cl_3$ (353.6), monoclinic, a = 830.3(4), b = 1352(1), c = 1516.9(7) pm; β = 124.75(3)°; V = 1399 × 10^6 pm^3; D(calc) = 1.68 g cm^{-3} with Z = 4. Space group $P2_1/c$. The intensities of 1520 independent reflections with $2° \leqslant 2\theta \leqslant 50°$ were collected by the ω-scan method.

Structure Determination

The structure was solved by the heavy atom method (Patterson), followed by one difference Fourier syntheses. The positions of the hydrogen atoms of the ethylenediamine ligands were calculated assuming ideal geometry. Atomic positions and thermal parameters of the nonhydrogen atoms were refined by full matrix least squares using anisotropic thermal parameters in the form $\exp[-\frac{1}{4}(h^2a^{*2}B11 + k^2b^{*2}B22 + l^2c^{*2}B33 + hka^*b^*B12 + hla^*c^*B13 + klb^*c^*B23)]$ (B_{ij} in 10^4 pm^2). The hydrogen atoms

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TABLE I. Atomic Coordinates of *cis*-[Co(en)$_2$(Im)Cl]Cl$_2$.

Name	X(SD)	Y(SD)	Z(SD)
Co	0.3678(1)	0.22691(7)	0.06124(8)
Cl1	1.0796(3)	0.1428(2)	0.2118(2)
Cl2	0.6127(3)	0.0907(1)	−0.1020(2)
Cl3	0.1360(3)	0.3440(2)	0.0086(1)
N11	0.1670(9)	0.1271(4)	0.0257(5)
C11	0.035(1)	0.1159(6)	−0.0929(6)
C12	0.156(1)	0.1226(6)	−0.1364(7)
N12	0.2909(9)	0.2069(4)	−0.0854(5)
N21	0.4366(8)	0.2363(5)	0.2081(5)
C21	0.569(1)	0.1520(7)	0.2729(6)
C22	0.699(1)	0.1330(6)	0.2361(6)
N22	0.5730(8)	0.1258(4)	0.1175(5)
N31	0.5588(9)	0.3259(4)	0.0852(5)
C32	0.584(1)	0.4144(6)	0.1314(6)
N33	0.715(1)	0.4674(5)	0.1270(5)
C34	0.782(1)	0.4116(6)	0.0793(6)
C35	0.6862(1)	0.3246(6)	0.0542(6)

were included in the final refinement with all their parameters fixed. The final difference Fourier syntheses indicates no significant residuals. Based on 1520 structure factors with $F_o \geqslant 3.98\sigma$ the agreement factors were $R_1 = 0.055$ and $R_2 = 0.057$.

The final parameters are given in Tables I and II*. Important bond lengths and bond angles are given in Tables III and IV.

TABLE III. Intramolecular Bond Distances in *cis*-[Co(en)$_2$-(Im)Cl]Cl$_2$ (in pm) with Standard Deviations in Parentheses.

Co–N11	196.6(7)
Co–N12	195.2(6)
Co–N21	196.3(6)
Co–N22	196.1(7)
Co–N31	194.5(7)
Co–Cl3	225.7(3)
N11–C11	149(1)
C11–C12	149(2)
C12–N12	147(1)
N21–C21	150(1)
C21–C22	150(2)
C22–N22	148(1)
N31–C32	134(1)
N31–C35	138(1)
C32–N33	134(1)
N33–C34	136(1)
C34–C35	135(1)
av. N–H(en)	110.2(7)
av. C–H(en)	110.5(9)
C32–H32	101(1)
N33–H33	107.5(6)
C34–H34	110(1)
C35–H35	115.0(9)

Description of the Structure and Discussion

Although the structures of some binary complexes of transition metals with imidazole of the type ML$_n$-X$_2$ have been determined [7], only relatively few structural investigations have been carried out with the ternary mixed ligand complexes involving imidazole [12–16]. The crystal structure of the title com-

TABLE II. Thermal Parameters of *cis*-[Co(en)$_2$(Im)Cl]Cl$_2$.

Name	B11	B22	B33	B12	B13	B23
Co	1.91(4)	1.62(4)	1.53(4)	−0.03(4)	1.14(4)	−0.11(4)
Cl1	2.84(9)	2.87(9)	2.49(9)	0.01(8)	1.81(8)	0.00(8)
Cl2	3.8(1)	2.21(9)	4.0(1)	0.35(8)	2.80(9)	0.37(8)
Cl3	2.72(9)	2.32(9)	3.4(1)	0.67(7)	1.78(8)	0.21(8)
N11	2.5(3)	2.5(3)	2.1(3)	−0.2(2)	1.4(3)	0.1(2)
C11	2.5(4)	4.3(5)	1.9(4)	−1.5(3)	1.1(3)	−1.1(3)
C12	2.7(4)	4.3(5)	2.5(4)	−1.2(3)	1.3(3)	−1.2(3)
N12	2.7(3)	2.7(3)	1.5(3)	−0.3(2)	1.2(2)	0.1(2)
N21	2.4(3)	2.5(3)	1.9(3)	−0.2(2)	1.4(2)	−0.3(2)
C21	3.6(4)	4.3(5)	1.7(4)	0.5(4)	1.4(3)	0.8(3)
C22	2.5(4)	4.1(4)	1.8(4)	0.3(3)	0.9(3)	−0.1(3)
N22	1.7(3)	2.3(3)	1.4(3)	0.1(2)	0.7(2)	−0.2(2)
N31	3.0(3)	1.5(3)	1.7(3)	0.1(2)	1.4(2)	0.2(2)
C32	3.2(4)	2.1(4)	2.8(4)	0.1(3)	1.7(3)	−0.1(3)
N33	3.3(3)	2.2(3)	2.5(3)	−0.3(3)	1.4(3)	−0.3(3)
C34	2.7(4)	2.9(4)	2.2(4)	−0.1(3)	1.2(3)	0.4(3)
C35	2.5(4)	2.6(4)	2.4(4)	−0.4(3)	1.6(3)	0.1(3)

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*The hydrogen atom coordinates together with structural factor tables may be obtained from the authors upon request.

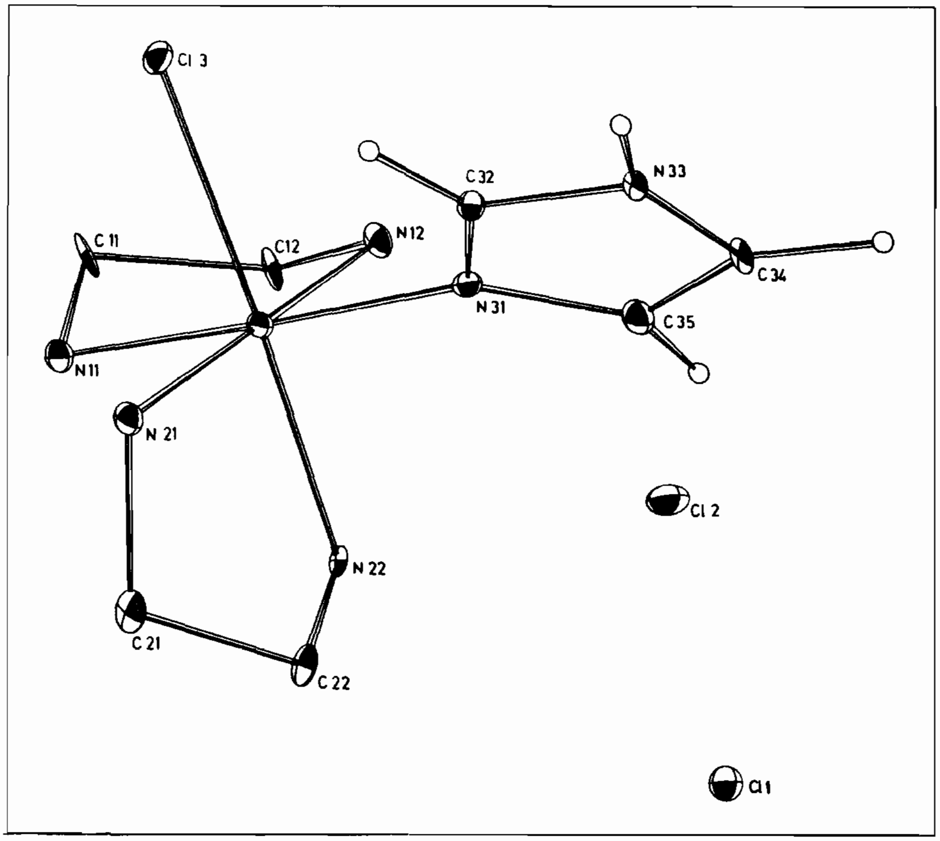
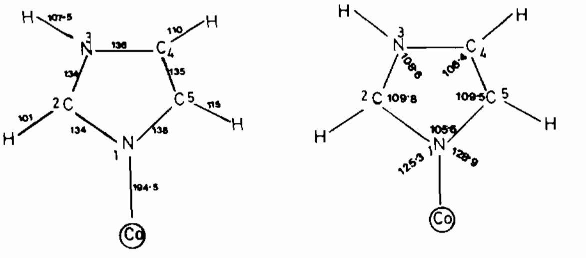


Fig. 1. A perspective drawing of *cis*-[Co(en)$_2$(Im)Cl]Cl$_2$. The ethylenediamine hydrogens are omitted for clarity.

TABLE IV. Intramolecular Bond Angles in *cis*-[Co(en)$_2$-(Im)Cl]Cl$_2$ (in degrees) with Standard Deviations in Parentheses.

N11–Co–C13	88.0(2)
N12–Co–Cl3	92.0(2)
N21–Co–Cl3	89.7(2)
N22–Co–Cl3	175.8(2)
N31–Co–C13	91.3(2)
N12–Co–N11	85.2(3)
N21–Co–N11	90.5(3)
N22–Co–N11	91.8(3)
N31–Co–N11	175.8(3)
N21–Co–N12	175.3(3)
N22–Co–N12	92.2(3)
N31–Co–N12	90.6(3)
N22–Co–N21	86.2(3)
N31–Co–N21	93.7(3)
N31–Co–N22	89.1(3)
C32–N31–Co	125.3(6)
C35–N31–Co	128.9(6)
C35–N31–C32	105.6(7)
N33–C32–N31	109.8(8)
C34–N33–C32	108.6(7)
C35–C34–N33	106.4(8)
C34–C35–N31	109.5(8)

pound was carried out to gain more information about these mixed ligand complexes. The crystal structure is shown in Fig. 1. In the crystal lattice of *cis*-[Co(en)$_2$(Im)Cl]Cl$_2$ the Co(III) containing cation shows octahedral geometry and is well separated from the two chloride ions (558.0 pm and 429.7 pm). The coordination sphere of cobalt is formed by one imidazole, one chloride ion and two ethylenediamine ligands. One ethylenediamine group spans equatorial–axial positions while the second one is bonded in an equatorial–equatorial way. The imidazole is coordinated through the pyridine nitrogen (⩾N) rather through the pyrrole nitrogen (>N–H). The coordination through the pyrrole nitrogen would result in the formation of a quaternary N-atom with a tetrahedral configuration. The X-ray crystal structure of free imidazole at –15 °C was carried out by Martinez-Carrera [17] and Freeman [18] calculated the average bond lengths for complexes imidazole rings. Our values are not much different from these values. The bond angles and bond distances or the complexed imidazole moiety in the complex under discussion are shown in Fig. 2. The imidazole ring is planar within standard deviations and includes an angle of 45° with the plane CoN11N12N21. The



(A) (B)

Fig. 2. Intramolecular bond distances (*A*) and bond angles (*B*) in the coordinated imidazole moiety of *cis*-$[Co(en)_2(Im)Cl]Cl_2$.

coordination octahedron shows a slight but significant distortion: the N(en)–Co–N(en) angles within the five-membered rings are smaller (85.2(3) and 86.2(3)) than those between two nitrogens belonging to different ethylenediamine ligands. The bridging carbon atoms of the ethylenediamine are located above and below the planes N(en)–Co–N(en). All Co–N and Co–Cl bond distances are in agreement with those in *trans*-$[Co(en)_2Cl_2][CoCl_4]$ and *cis*-$[Co(en)_2(NCS)_2]Cl$ [12], *trans*-$[Co(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O$ [19], *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$ [20], *trans*-$[Co(en)_2Cl_2]Cl$ [21] and *trans*-$[Co(en)_2Cl_2](NO_3)$ [22].

Some kind of *trans*-effect of either the chloride ion or the imidazole ligand cannot be observed, all the Co–N bond distances being approximately equal within standard deviations.

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