Inorganica Chimica Acta, 39 (1980) 181–186

Spectroscopic Study and X-ray Structure of Tetra(N-methylimidazole)platinum(II) Hexachloroplatinate(IV)

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Received July 23, 1979

The crystal structure of $Co(NMIz)_2(tcf)_2$ *(NMIz = N-methylimidazole; tcf = 2,4,6-trichlorophenolate) has been determined by X-ray diffraction methods. The compound crystallizes in space group* $P\bar{1}$ *with cell parameters:* $a = 11.783(8)$, $b = 14.461(9)$, $c = 8.569(7)$ Å, $\alpha = 91.45(6)$, $\beta = 103.68(8)$, $\gamma = 117.58(8)^\circ$ *and* $Z = 2$ *for* $D_c = 1.65$ g cm^{-3}.

Room temperature intensity data were obtained with a Siemens AED automated single-crystal diffractometer using Nb-filtered Mo-Kα radiation (λ = 0.71069 Å). The final R-factor, based upon 1439 observed reflections, was 0.041. The structure consists of monomeric units $Co(tcf)_2(NMIz)_2$*, in which Co(II) is coordinated by two oxygen atoms of tcf and two nitrogen atoms from NMIz in a distorted tetrahedral arrangement. Co–O bond distances are 1.889 and 1.898 Å, and Co–N bond distances are 2.011 and 2.026 Å. A chlorine from one of the tcf ligands involved in a long Co–Cl bond of 3.100 Å completes the distorted five coordination around the metal. Solid-state and solution ligand-field spectra are identical and agree with five-coordinated high-spin Co(II). Conductivity data and molecular weight determination in solution both agree with a monomeric species. NMR spectra in solution in the presence of additional NMIz and tcfH indicate a rapid ligand exchange process on the NMR time scale.*

Introduction

In metalloproteins coordination of transition metal ions by imidazole side chains of histidine and by phenol side chains of tyrosine is well documented [1], although the detailed coordination geometry around the metal ions is known in only a few cases [2]. Coordination of both imidazoles and phenoles is known to occur in *e.g.* transferrine, laccase and hemerythrin. Model coordination compounds containing this type of ligands could be of help in further understanding and investigating the structure of such metalloproteins. As part of an investigation studying the coordination of first-row transition metal ions by imidazoles and phenol ligands, several unusual coordination compounds have been found, having distorted coordination geometries for the metal ions.

The present paper describes the synthesis, characterisation, spectroscopic studies and crystal structure of one example of this class of compounds, $Co(NMIz)_2(tcf)_2$ (NMIz = N-methylimidazole; tcf = 2,4,6-trichlorophenolate).

Experimental

Starting Materials

N-methyl imidazole was commercially available from Aldrich and was used without further purification. $CoSO_4(H_2O)_6$ and trichlorophenol were also commercially available.

Preparation and Analyses

The title compound was prepared as described elsewhere [3]. By using a delicate balance between water and acetone as solvents, the compound beautifully crystallizes as deep purple needles. The crystals were analysed with respect to their content of Co, C, H and N using standard techniques. A molecular weight determination was carried out by vapour pressure osmometry in acetone (Malissa and Reuter, Engelskirchen, Germany). Ligand-field spectra were obtained as described earlier [3]. NMR spectra were recorded on a Varian T-60 instrument.

Crystal Data

A rather flattened dark purple crystal (of dimensions *ca.* 0.05 × 0.15 × 0.35 mm) was used for the X-ray analysis. The unit cell parameters were determined first from rotation and Weissenberg photographs and then refined from a least-square procedure

TABLE I. Fractional Atomic Coordinates (× 10^4 for Co, Cl, O, N, C atoms; × 10^3 for H atoms) and Thermal Parameters (× 10^3) with e.s.d.'s in Parentheses.[a]

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	5210(1)	2563(1)	2532(2)	42(1)	42(1)	43(1)	6(1)	9(1)	20(1)
Cl(1)	8781(3)	2095(2)	2531(4)	56(2)	57(2)	61(2)	19(2)	9(2)	26(2)
Cl(2)	9916(3)	4301(3)	−2341(4)	59(2)	80(2)	68(2)	27(2)	33(2)	34(2)
Cl(3)	5339(3)	3263(2)	−840(4)	52(2)	67(2)	71(2)	17(2)	20(2)	35(2)
Cl(4)	2492(4)	225(3)	826(4)	113(3)	87(3)	71(3)	31(2)	15(2)	67(2)
Cl(5)	−827(4)	669(3)	−4230(4)	80(2)	110(3)	62(2)	−1(2)	−13(2)	43(2)
Cl(6)	2840(4)	4001(3)	226(5)	71(3)	57(2)	133(4)	−6(2)	−1(2)	30(2)
O(11)	6284(7)	2191(5)	1608(8)	44(5)	38(5)	49(5)	10(4)	16(4)	13(4)
O(12)	3519(7)	2484(6)	1819(10)	42(5)	88(7)	56(6)	−13(5)	6(4)	31(5)
N(13)	4948(9)	985(6)	6569(10)	69(7)	36(5)	30(6)	−3(4)	14(5)	8(5)
N(33)	5304(8)	1808(6)	4458(10)	41(5)	46(6)	38(5)	−3(4)	4(4)	19(5)
N(14)	7009(9)	5752(7)	4435(11)	63(7)	39(6)	55(6)	−1(5)	19(5)	7(5)
N(34)	6361(8)	4113(6)	3494(11)	51(6)	30(5)	60(6)	−3(5)	5(5)	13(5)
C(11)	7101(11)	2693(8)	742(13)	42(8)	33(7)	38(7)	10(6)	7(6)	10(6)
C(21)	8318(10)	2703(8)	955(12)	44(7)	38(7)	37(7)	−1(5)	−2(5)	18(6)
C(31)	9166(11)	3195(8)	29(13)	38(8)	44(7)	54(7)	7(5)	13(6)	17(6)
C(41)	8836(10)	3708(8)	−1158(12)	51(7)	49(7)	45(7)	17(6)	19(6)	24(6)
C(51)	7674(11)	3753(8)	−1418(14)	58(7)	48(8)	49(6)	2(6)	14(6)	33(6)
C(61)	6830(10)	3238(8)	−471(13)	54(7)	49(7)	37(7)	−1(6)	11(6)	31(6)
C(12)	2572(11)	2081(10)	468(15)	32(7)	64(9)	56(8)	6(7)	21(7)	25(7)
C(22)	1935(11)	1018(9)	−213(13)	57(8)	54(8)	45(7)	14(6)	22(6)	20(7)
C(32)	887(12)	556(11)	−1624(13)	56(8)	58(10)	43(7)	−4(7)	2(6)	24(7)
C(42)	472(11)	1198(9)	−2426(13)	43(7)	71(9)	49(7)	3(6)	1(6)	32(7)
C(52)	1049(10)	2250(10)	−1875(14)	41(7)	64(9)	64(8)	23(7)	6(6)	27(6)
C(62)	2077(11)	2649(9)	−472(15)	45(7)	44(8)	75(9)	5(7)	25(7)	20(6)
C(23)	4477(13)	1370(8)	5341(13)	54(9)	43(7)	51(7)	5(5)	12(7)	20(7)
C(43)	6390(12)	1688(9)	5187(14)	52(9)	45(7)	50(8)	18(6)	11(7)	16(7)
C(53)	6179(11)	1201(8)	6473(15)	61(8)	46(7)	52(9)	6(6)	3(7)	29(6)
C(63)	4258(17)	450(12)	7755(18)	100(13)	71(10)	66(10)	28(8)	36(9)	17(10)
C(24)	6024(13)	4855(8)	3539(14)	48(9)	48(7)	63(8)	9(6)	14(7)	17(6)
C(44)	7665(12)	4567(11)	4451(14)	47(8)	52(10)	62(8)	3(7)	3(6)	9(7)
C(54)	8041(13)	5564(11)	5006(16)	44(9)	56(10)	74(9)	−6(8)	−1(7)	−1(8)
C(64)	6975(20)	6729(11)	4766(22)	142(16)	40(8)	96(13)	−1(9)	53(12)	36(10)
H(31)	995(9)	314(7)	19(10)	40(30)					
H(51)	741(9)	419(7)	−236(11)	80(30)					
H(32)	40(9)	−19(8)	−199(12)	70(30)					
H(52)	78(9)	266(7)	−243(11)	70(30)					
H(23)	368(9)	130(7)	507(11)	50(30)					
H(43)	730(9)	196(7)	476(11)	60(30)					
H(53)	687(9)	100(7)	732(11)	50(30)					
H(631)	478(10)	26(8)	834(13)	190(40)					
H(632)	324(11)	−17(9)	710(12)	170(30)					
H(633)	403(10)	83(9)	836(13)	200(40)					
H(24)	501(10)	474(7)	288(12)	50(30)					
H(44)	828(9)	416(7)	470(11)	100(30)					
H(54)	904(10)	614(8)	580(12)	110(30)					
H(641)	765(12)	723(10)	518(14)	180(40)					
H(642)	635(12)	669(9)	539(14)	180(40)					
H(643)	681(11)	692(9)	368(15)	170(40)					

[a] Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + U_{12}hka^*b^*)]$.

applied to the θ values of 16 reflections accurately measured on a Siemens AED automated single-crystal diffractometer. The most significant crystal data are as follows: $C_{20}H_{16}Cl_6CoN_4O_2$, M.W. = 616.02, triclinic, a = 11.783(8), b = 14.461(9), c = 8.569(7) Å, α = 91.45(6), β = 103.68(8), γ = 117.58(8)°, V = 1242(2) Å^3, Z = 2, D_c = 1.65 g cm^{-3}, μ(Mo-Kα) = 13.66 cm^{-1}; space group: $P\bar{1}$.

Intensity data were collected at room temperature using the same diffractometer with the Nb-filtered

Mo-Kα radiation (λ = 0.710688 Å). 2661 independent reflections with $2.5 < \theta < 21.0°$ were measured, 1439 of them were labelled as observed and used in the analysis having $I > 2\sigma(I)$. A standard reflection was periodically measured after every 20 reflections to check the stability of the sample and of the instrument. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made. The first absolute scaling and the overall isotropic temperature factor were obtained by Wilson's method.

The structure was solved by Patterson and Fourier methods and refined by least-squares full-matrix cycles using the SHELX system of computer programs [4] with initially isotropic and then anisotropic thermal parameters. A final ΔF map gave the positions of all the hydrogen atoms. Further least-squares cycles were then computed including these hydrogen atoms with isotropic thermal parameters. Unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to $|F_0|$. The final R was 0.041 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Co and Cl) were taken from the International Tables [5]. The atomic fractional coordinates and thermal parameters are listed in Table 1. A list of observed and calculated structure factors is available from the authors, on request. All the calculations were performed on the CYBER 76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

Results and Discussion

Crystal and Molecular Structure

The structure of the complex is represented in Fig. 1. Bond distances and angles are given in Table II. The cobalt is surrounded by a distorted tetrahedral arrangement of nitrogen atoms from two N-methylimidazole molecules and of oxygen atoms from two trichlorophenoxy groups. The Co–N bonds [2.011(9) and 2.026(9) Å] are in good agreement with those found in the crystal structure of bis(5,5-diethylbarbiturato)bisimidazolecobalt(II) [6] and the Co–O bonds [1.889(8) and 1.898(8) Å] are intermediate between those usually reported for tetrahedral and square-planar configurations of Co^{2+}, (2.06 and 1.86 Å respectively [7]).

The Cl(3) atom from one of the trichlorophenoxy ligands I is involved in a long contact with the cobalt atom [Co–Cl(3) = 3.100(4) Å]. Though this distance is too long to be regarded as an usual coordination bond, the chlorine atom is located to form a distorted square pyramid around Co, with the nitrogen atom N(34) at the apex of the pyramid. The cobalt atom is displaced from the mean basal plane passing through O(11), O(12), N(33) and Cl(3) by 0.382(2) Å towards the apex of the pyramid (Table III). Taking this contact into account the trichlorophenoxy group I can be considered as a bidentate chelating ligand. The first example of coordination to a transition metal by a phenyl chlorine atom has been found in the crystal structure of bis(1-methyl-3-*o*-chlorophenyltriazene 1-oxide)cobalt(II) [8], where two chlorine atoms are weakly coordinated to the metal [Co–Cl = 2.943 and 3.016 Å] in a severely distorted octahedral arrangement. The chlorine atom Cl(4) from the other trichlorophenoxy ligand II occupies the sixth octahedral site of the cobalt atom at a distance of 3.367(5) Å, much longer than that formed by the Cl(3) atom. The angles formed by the Co...Cl(4) direction with the other bonds in the coordination polyhedron are: Cl(4)–Co–O(12) 60.2, Cl(4)–Co–N(33) 82.6, Cl(4)–Co–O(11) 91.3, Cl(4)–Co–Cl(3) 91.6, Cl(4)–Co–N(34) 160.6°.

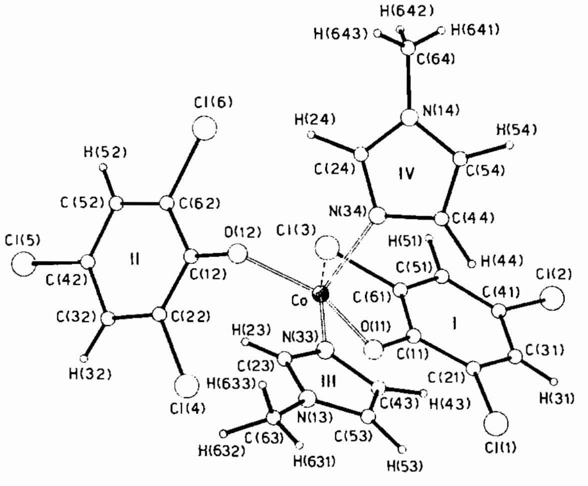

Fig. 1. Molecular structure of Co(NMIz)$_2$(tcf)$_2$ showing the atomic numbering scheme and the coordination around Co(II).

The geometries of the two trichlorophenoxy groups are not significantly different and those of the two imidazole molecules, not significantly different, are close to those found in the crystal structures of related NMIz compounds [9]. The trichlorophenoxy groups and the N-methylimidazole molecules are roughly planar (Table III), the maximum deviation from the mean planes through them being of 0.074 Å for O(11) from ligand I, 0.054(8) for O(12) from ligand II, 0.08 and 0.011 Å for C(53) and C(64) from the two imidazole molecules III and IV respectively. The trichlorophenoxy group I is almost coplanar with the adjacent N-methylimidazole ligand III (the dihedral angle being 5.1°), while the trichlorophenoxy group II forms an angle of 28.9° with the adjacent N-methylimidazole ligand IV. The configuration of the complex would seem to be stabilized by

TABLE II. Bond Distances (Å) and Angles (°).

In the coordination polyhedron			
Co–O(11)	1.898(8)	Co–N(33)	2.011(9)
Co–O(12)	1.889(8)	Co–Cl(3)	3.100(4)
Co–N(34)	2.026(9)		
O(11)–Co–N(34)	105.9(3)	N(33)–Co–N(34)	104.0(4)
N(34)–Co–O(12)	100.6(4)	Cl(3)–Co–O(11)	67.5(2)
O(11)–Co–O(12)	136.7(3)	Cl(3)–Co–O(12)	80.6(3)
N(33)–Co–O(11)	95.8(3)	Cl(3)–Co–N(34)	86.9(3)
N(33)–Co–O(12)	110.4(4)	Cl(3)–Co–N(33)	162.2(3)
In the trichlorophenoxy groups			
C(11)–C(21)	1.395(17)	C(12)–C(22)	1.395(20)
C(21)–C(31)	1.371(16)	C(22)–C(32)	1.386(16)
C(31)–C(41)	1.362(17)	C(32)–C(42)	1.366(21)
C(41)–C(51)	1.367(17)	C(42)–C(52)	1.361(20)
C(51)–C(61)	1.389(16)	C(52)–C(62)	1.369(17)
C(61)–C(11)	1.386(17)	C(62)–C(12)	1.385(20)
C(11)–O(11)	1.312(14)	C(12)–O(12)	1.295(15)
C(21)–Cl(1)	1.746(12)	C(22)–Cl(4)	1.735(14)
C(41)–Cl(2)	1.740(11)	C(42)–Cl(5)	1.748(12)
C(61)–Cl(3)	1.728(12)	C(62)–Cl(6)	1.746(15)
C(31)–H(31)	0.94(10)	C(32)–H(32)	0.96(12)
C(51)–H(51)	1.11(10)	C(52)–H(52)	0.89(11)
C(11)–C(21)–C(31)	123.0(1.1)	C(12)–C(22)–C(32)	124.9(1.3)
C(21)–C(31)–C(41)	119.9(1.1)	C(22)–C(32)–C(42)	117.3(1.4)
C(31)–C(41)–C(51)	120.5(1.0)	C(32)–C(42)–C(52)	122.1(1.1)
C(41)–C(51)–C(61)	118.1(1.1)	C(42)–C(52)–C(62)	117.2(1.3)
C(51)–C(61)–C(11)	124.1(1.1)	C(52)–C(62)–C(12)	126.3(1.3)
C(61)–C(11)–C(21)	114.2(1.0)	C(62)–C(12)–C(22)	112.1(1.1)
O(11)–C(11)–C(21)	122.1(1.0)	O(12)–C(12)–C(22)	123.6(1.3)
O(11)–C(11)–C(61)	123.6(1.1)	O(12)–C(12)–C(62)	124.3(1.3)
Cl(1)–C(21)–C(11)	117.3(8)	Cl(4)–C(22)–C(12)	116.6(9)
Co–O(11)–C(11)	131.1(8)	Co–O(12)–C(12)	133.4(9)
Cl(1)–C(21)–C(31)	119.6(9)	Cl(4)–C(22)–C(32)	118.4(1.1)
Cl(2)–C(41)–C(31)	118.9(9)	Cl(5)–C(42)–C(32)	119.6(1.0)
Cl(2)–C(41)–C(51)	120.6(9)	Cl(5)–C(42)–C(52)	118.3(1.0)
Cl(3)–C(61)–C(51)	118.1(9)	Cl(6)–C(62)–C(12)	116.2(1.0)
Cl(3)–C(61)–C(11)	117.8(9)	Cl(6)–C(62)–C(52)	117.5(1.1)
H(31)–C(31)–C(21)	119(6)	H(32)–C(32)–C(22)	123(6)
H(31)–C(31)–C(41)	121(6)	H(32)–C(32)–C(42)	119(6)
H(51)–C(51)–C(41)	121(5)	H(52)–C(52)–C(42)	121(6)
H(51)–C(51)–C(61)	121(5)	H(52)–C(52)–C(62)	122(6)
In the N-methylimidazole molecules			
N(13)–C(23)	1.328(15)	N(14)–C(24)	1.324(16)
C(23)–N(33)	1.313(16)	C(24)–N(34)	1.308(17)
N(33)–C(43)	1.375(16)	N(34)–C(44)	1.381(15)
C(43)–C(53)	1.334(18)	C(44)–C(54)	1.332(24)
C(53)–N(13)	1.359(15)	C(54)–N(14)	1.350(18)
N(13)–C(63)	1.463(19)	N(14)–C(64)	1.454(22)
C(23)–H(23)	0.87(10)	C(24)–H(24)	1.12(11)
C(43)–H(43)	1.11(10)	C(44)–H(44)	1.11(11)
C(53)–H(53)	1.11(10)	C(54)–H(54)	1.11(11)
C(63)–H(631)	0.85(12)	C(64)–H(641)	0.78(13)
C(63)–H(632)	1.10(12)	C(64)–H(642)	0.99(13)
C(63)–H(633)	0.91(13)	C(64)–H(643)	0.98(13)

(Continued on facing page)

TABLE II. *(Continued)*

N(13)–C(23)–N(33)	113.3(1.1)	N(14)–C(24)–N(34)	112.5(1.1)
C(23)–N(33)–C(43)	104.1(1.0)	C(24)–N(34)–C(44)	105.3(1.1)
N(33)–C(43)–C(53)	109.4(1.1)	N(34)–C(44)–C(54)	107.7(1.3)
C(43)–C(53)–N(13)	107.8(1.1)	C(44)–C(54)–N(14)	108.8(1.2)
C(53)–N(13)–C(23)	105.4(1.0)	C(54)–N(14)–C(24)	105.7(1.2)
C(53)–N(13)–C(63)	128.6(1.1)	C(64)–N(14)–C(24)	127.1(1.2)
C(23)–N(13)–C(63)	126.0(1.2)	C(64)–N(14)–C(54)	127.2(1.3)
Co–N(33)–C(23)	132.4(8)	Co–N(34)–C(24)	129.3(8)
Co–N(33)–C(43)	123.5(8)	Co–N(34)–C(44)	124.9(9)
H(23)–C(23)–N(13)	125(6)	H(24)–C(24)–N(14)	124(6)
H(23)–C(23)–N(33)	121(6)	H(24)–C(24)–N(34)	123(6)
H(43)–C(43)–N(33)	125(5)	H(44)–C(44)–N(34)	125(5)
H(43)–C(43)–C(53)	126(5)	H(44)–C(44)–C(54)	127(5)
H(53)–C(53)–C(43)	127(5)	H(54)–C(54)–C(44)	125(7)
H(53)–C(53)–N(13)	125(5)	H(54)–C(54)–N(14)	126(7)

TABLE III. Equations of Least-squares Planes are in the Form: $AX + BY + CZ = D$, where X, Y and Z are coordinates in Å referred to orthogonal axes, and obtained from fractional ones by applying the matrix: $\|a\sin\gamma, 0, -c\sin\alpha\cos\beta^*|a\cos\gamma, b, c\cos\alpha|0,0, c\sin\alpha\sin\beta^*\|$. Deviations (Å) of relevant atoms from the planes are in square brackets.

	A	*B*	*C*	*D*
Plane I: C(11) C(21) C(31) C(41) C(51) C(61) Cl(1) Cl(2) Cl(3) O(11) [C(11) 0.019(12), C(21) 0.022(12), C(31) 0.007(12), C(41) –0.017(12), C(51) –0.051(12), C(61) –0.021(12), Cl(1) –0.018(3), Cl(2) 0.001(4), Cl(3) –0.015(3), O(11) 0.074(8)]	–0.2849	–0.7087	–0.6455	–2.4779
Plane II: C(12) C(22) C(32) C(42) C(52) C(62) Cl(4) Cl(5) Cl(6) O(12) [C(12) –0.018(12), C(22) 0.010(12), C(32) – 0.001(12), C(42) –0.004(12), C(52) –0.004(11), C(62) 0.004(12), Cl(4) 0.027(4), Cl(5) 0.010(4), Cl(6) 0.030(4), O(12) –0.054(8)]	0.8382	–0.1292	–0.5298	1.7650
Plane III: N(13) C(23) N(33) C(43) C(53) C(63) [N(13) 0.001(9), C(23) –0.003(13), N(33) –0.001(9), C(43) 0.007(13), C(53) –0.008(13), C(63) 0.004(18)]	–0.2511	–0.7690	–0.5879	–2.9879
Plane IV: N(14) C(24) N(34) C(44) C(54) C(64) [N(14) 0.007(9), C(24) 0.001(12), N(34) 0.002(9), C(44) –0.003(12), C(54) 0.005(14), C(64) –0.011(19)]	0.5662	0.1863	–0.8029	1.4256
Plane V: O(11) N(33) O(12) Cl(3) [O(11) 0.150(8), N(33) –0.248(9), O(12) 0.129(9), Cl(3) –0.031(3), Co –0.382(2), N(34) –2.376(9)]	–0.4782	–0.6909	–0.5422	–3.6172

two intramolecular C–H...Cl interactions, involving carbon atoms of imidazole and chlorine atoms H(24)...Cl(6) = 2.73(10) Å, C(24)–H(24)–Cl(6) = 152(7)°; H(43)...Cl(1) = 2.83(9) Å, C(43)–H(43)–Cl(1) = 156(7)°. Other intermolecular C–H...Cl interactions, together with normal van der Waals contacts, can play a significant role in determining the packing [H(53)...Cl(4) $(1 - x, -y, 1 - z)$ = 2.65(11) Å, C(53)–H(53)–Cl(4) $(1 - x, -y, 1 - z)$ = 155(7)°; H(54)...Cl(1) $(2 - x, 1 - y, 1 - z)$ = 2.68(11) Å, C(54)–H(54)–Cl(1) $(2 - x, 1 - y, 1 - z)$ = 164(9)°]. Since the sum of the van der Waals radii of hydrogen and chlorine atoms is 3.0 Å, the H...Cl distances (less than 3.0 Å) and the geometry of these C–H...Cl interactions suggest that attractive H...Cl forces are present, which are slightly stronger than the usual van der Waals effects. The packing of the molecules is shown in Fig. 2.

Solution Properties and Spectroscopic Data

The crystal structure has revealed that the coordination polyhedron around Co(II) has a distorted

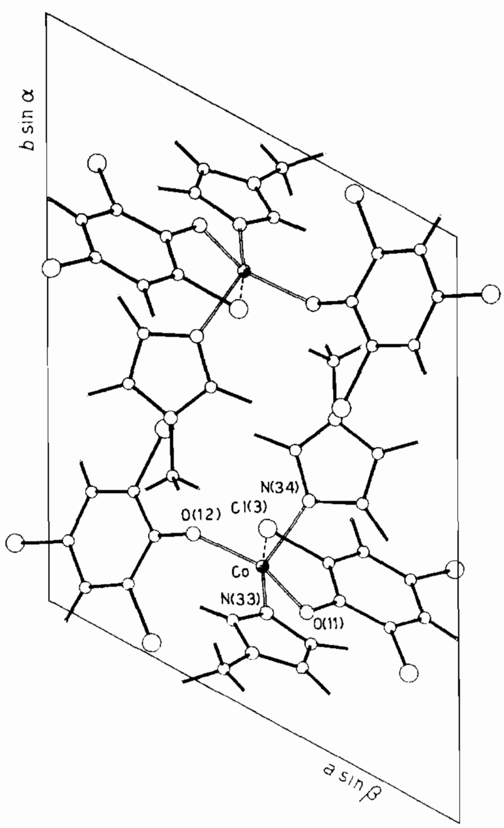

Fig. 2. Projection of the structure of Co(NMIz)$_2$(tcf)$_2$ along the *c* axis, showing the packing of the molecular complexes.

square-pyramidal geometry, which is unusual in the sense that the Cl atom of one of the tcf anions is able to coordinate to the metal ion. Previous work [3] has shown that the corresponding compounds M(tcf)$_2$-(NMIz)$_2$ (M = Ni, Cu, Zn) have infrared and far-IR spectral data that are very much the same compared with the present compound, suggesting the same coordination geometry for the metal ions.

Because preliminary solubility studies indicated that the colour of the Co(II) compound is retained in solution of apolar solvents, we decided to carry out a more detailed solution study, to see whether or not decomposition, solvation and/or association occurs. In Table IV, some data have been listed. It is clear that the differences in ligand-field maxima for the solid and the dissolved Co(II) compound are minor, suggesting the presence of the same molecular species in either case [10]. The small differences at best indicate small differences on bond angles around cobalt. The fact that no marked reaction occurs with the solvent molecules indicates that this distorted five-coordinate geometry around Co(II) is quite stable with respect to ligand exchange and ligand addition.

Since Co(II) high-spin complexes are known to be labile with respect to ligand exchange [11], we decided to investigate this by proton NMR spectroscopy. Therefore NMR spectra were recorded in acetone-d$_6$ in the presence of an excess of either NMIz and tcfH. In case of a slow ligand exchange process (with respect to the NMR time-scale) between free and coordinated NMIz and between free and coordinated tcf, separate signals should be observed for complexed, paramagnetic and for free, diamagnetic species [11]. In fact only one set of NMIz and tcf signals is observed, in agreement with a rapid ligand exchange process on the NMR time scale. As expected, the line positions are dependent upon the relative amounts of paramagnetic and diamagnetic species. So, even though the ligands around Co(II) do exchange rapidly, the predominant species in solution is nevertheless the uncommon, five-coordinated one.

TABLE IV. Spectroscopic and Solution Data of Co(NMIz)$_2$-(tcf)$_2$.

Ligand-field Maxima^a		Molecular Weight in Acetone (0.01–0.03 *M*):
(solid state)	(2.5 mmol/l in acetone)	572–578 (calc. 616)
6.5	6.8(30)^b	Conductivity in Acetone (0.0012 *M*):
7.5	8.0(30)	
10.8	11.4(30)	0.5 Ω^{-1} cm^2 mol^{-1}
15.8	15.9(290)	
18.5	19.2(320)	

^{a}Band maxima in kK. $^b\epsilon$ values in parentheses.

Acknowledgements

The authors are indebted to dr. ir. J. A. M. van Hest for discussions and for critically reading the manuscript.

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