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Complexes of Cobalt(II) with α-Diimines. The Crystal Structure of $CoCl_2$(t-Bu–N=CH–CH=N–t-Bu)

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Complexes of Co(II) with α-diimines, of general formula CoX_2(R–N=CH–CH=N–R) (X = Cl, Br; R = benzyl, cyclohexyl, isopropyl, terbutyl) and $CoX_2(R{-}N{=}CH{-}CH{=}N{-}R)_2$ (X = Cl, Br; R = phenyl) were prepared and characterized. In all the complexes the α-diimine ligand is chelating and the nature of the R substituent seems to determine the tetrahedral or octahedral coordination of the CoX_2(R–N=CH–CH=N–R) or $CoX_2(R{-}N{=}CH{-}CH{=}N{-}R)_2$ complexes respectively. The structure of the $CoCl_2$(t-Bu-DAB) has been determined. The Co atom presents a distorted tetrahedral coordination. The crystals are monoclinic, space group $P2_1$ with a *= 7.002(1),* b *= 10.234(3),* c *= 10.728(4) Å, β = 105.48(1)°,* V *= 740.8(6) Å^3,* M_r *= 297.8,* Z *= 2,* D_c *= 1.34 Mg m^{-3}. The atomic parameters have been refined by least squares analysis of 1365 observed reflexions to a R value of 0.047.*

Introduction

The use of α-diimines RN=CR′–CR′=NR (R-DAB) as ligands to obtain transition metal complexes has received a great deal of attention in recent years, importance being related to their versatile coordination behaviour [1–4]. The type of branching at the C_α and C_β atoms of the imine R substituents, as well as the nature of RR′ substituents, seem to be important factors which determine the stability of the α-diimine–metal interaction and the coordination mode [2, 4].

Although many studies on cobalt complexes with dihydrazones as ligands of general formula $CoX_2(DAB)_n$ (n = 1, 2, 3) have been made [5–9], the literature about the analogous cobalt α-diimine complexes is scarce [10–13] when compared with the abundant literature on transition metal complexes with α-diimines [1, 12–14].

The investigations reported here are concerned with the preparation methods and characterization of Co(II) complexes with α-diimines. The ligands selected for this investigation were glyoxalbis(tert-butylimine) (t-Bu-DAB), glyoxalbis(benzylimine) (Bz-DAB), glyoxalbis(phenylimine) (Ph-DAB), glyoxalbis(cyclohexylimine) (c-Hex-DAB) and glyoxalbis(isopropylimine) (i-Pr-DAB), in order to understand the influence of the R substituent on the coordination mode. The crystal structure of the compound with maximum branching at C_α in R, $CoCl_2$(t-Bu-DAB), has been determined.

Experimental

The α-diimines RN=CH–CH=NR [R = CH_2-C_6H_5, C_6H_5, C_6H_{11}, $CH(CH_3)_2$ and $C(CH_3)_3$] were synthesized by standard methods from glyoxal, benzylamine, cyclohexylamine, isopropylamine and tert-butylamine (Merck).

All preparations were carried out in a dry, oxygen-free, nitrogen atmosphere, or *in vacuo*, using standard Schlenk techniques. When it was necessary, solvents were dried by standard methods prior to use.

Elemental analyses for C, H and N were performed by Elemental Microanalysis Limited, Devon (England). Infrared spectra in the 4000–200 cm^{-1} region were recorded as KBr discs or Nujol mulls between CsI plates on a Perkin-Elmer 325 spectrometer. Electronic spectra were recorded on a Kontron-Uvikon 820 spectrometer, using acetone as solvent. Magnetic susceptibilities were determined by the Gouy method, using a 4411 Sartorius electronic microbalance, a B-M-4 Bruker magnet and a VNK 3-300 Leybold-Heraeus cryostat. Molar con-

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ductivities were measured with a Philips 6M 4144/01 conductivity bridge, using a PR 9512/00 measurement cell.

Preparation of Complexes

CoX_2(t-Bu-DAB) (X = Cl, Br)

a) A suspension of $CoCl_2(PPh_3)_2$ (1.31 g, 2 mmol) in acetone (100 ml) was treated with t-Bu-DAB (0.34 g, 2 mmol). The blue solution turned quickly to green. The mixture was stirred for 30 min. After filtration of the solution the solvent was removed leaving a green solid, which was filtered off, washed with diethyl ether several times, and recrystallized from acetone (yield 90%).

b) Following the previous procedure by addition of t-Bu-DAB (0.34 g, 2 mmol) to a solution of anhydrous $CoCl_2$ (0.26 g, 2 mmol) in dry acetone (100 ml) the same compound was obtained (yield 95%).

$CoBr_2$(t-Bu-DAB) was obtained by both methods with similar results.

When the reactions were carried out in 1:2 molar ratio (Co:L) the same results were obtained.

CoX_2(Bz-DAB) (X = Cl, Br)

a) To a suspension of $CoCl_2(PPh_3)_2$ (0.65 g, 1 mmol) in acetone (100 ml) was added Bz-DAB (0.23 g, 1 mmol). The initially blue solution turned slowly to green. After stirring for 2 h at room temperature, the solvent was completely removed leaving a green oil. The treatment of this oil with diethyl ether gave a green solid, which was filtered off, washed with diethyl ether and dried *in vacuo* (yield 65%).

b) Following the above procedure, by addition of Bz-DAB (0.47 g, 2 mmol) to a solution of anhydrous $CoCl_2$ (0.26 g, 2 mmol) in dry acetone (100 ml), the same compound was isolated (yield 70%).

$CoBr_2$(Bz-DAB) was obtained by both methods with similar results.

When the reactions were carried out in 1:2 molar ratio (Co:L) the same results were obtained.

CoX_2(Ph-DAB)$_2$ (X = Cl, Br)

a) $CoCl_2(PPh_3)_2$ (0.65 g, 1 mmol) in acetone (100 ml) was treated with Ph–DAB (0.42 g, 2 mmol) and the mixture was stirred for 2 h at room temperature. The initially blue solution became briefly green before turning purple. After filtration of the solution the solvent was removed, leaving a purple oil. By addition of diethyl ether a purple solid appeared, which was filtered off, washed with diethyl ether and dried *in vacuo* (yield 80%).

b) Following the above procedure Ph-DAB (0.42 g, 2 mmol) was added to a solution of anhydrous $CoCl_2$ (0.13 g, 1 mmol) in dry acetone (100 ml). The same compound was obtained (yield 80%).

$CoBr_2$(Ph-DAB)$_2$ was synthesized by both methods with similar results.

When the reactions were carried out in 1:2 molar ratio (Co:L) the same compounds were obtained.

CoX_2(c-Hex-DAB) (x = Cl, Br)

a) $CoCl_2(PPh_3)_2$ (1.30 g, 2 mmol) in acetone (50 ml) was treated with c-Hex-DAB (0.44 g, 2 mmol). The blue solution turned quickly to green. The mixture was stirred for 30 min giving a bright green precipitate, which was filtered off, washed with diethyl ether and dried *in vacuo*. By concentration of the filtrate more solid was obtained (Total yield 65%).

b) Following the previous procedure, by addition of c-Hex-DAB (0.88 g, 4 mmol) to a solution of anhydrous $CoCl_2$ (0.52 g, 4 mmol) in dry acetone (50 ml) the same compound was isolated, (yield 75%).

$CoBr_2$(c-Hex-DAB) was prepared similarly by both methods.

When the reactions were carried out in 1:2 molar ratio (Co:L) the same results were obtained.

CoX_2(i-Pr-DAB) (X = Cl, Br)

a) A suspension of $CoCl_2(PPh_3)_2$ (0.65 g, 1 mmol) in acetone (100 ml) was treated with i-Pr-DAB (0.14 g, 1 mmol) and the mixture was stirred at room temperature for 30 min. The initially blue solution turned quickly to green. The solvent was removed under reduced pressure leaving a green oil, which was treated with diethyl ether to give a green solid (yield 60%).

b) Following the previous procedure, by addition of i-Pr-DAB (0.42 g, 3 mmol) to a solution of anhydrous $CoCl_2$ (0.39 g, 3 mmol) in dry acetone (100 ml) the same compound was isolated (yield 65%).

The reactions in 1:2 molar ratio (Co:L) gave the same results.

$CoBr_2$(i-Pr-DAB) was prepared similarly by both methods.

X-Ray Data Collection

A green crystal was mounted on a Nonius CAD4-F diffractometer. All the dimensions were refined by least-squares fitting of the θ values of 21 reflexions. The intensities of 2798 unique reflexions with $1 < \theta < 32°$ were measured at 295 °K with monochromatic MoK_α radiation (λ = 0.71069 Å) and a w/2θ scan technique. There was no appreciable change in the periodically monitored standard reflexions.

The systematic absences were 0k0 for k odd. The two possible space groups are $P2_1$ and $P2_1/m$. The intensities were corrected for Lorentz and polarization effects and 1365 of these were considered as

TABLE I. Coefficients for the Weighting Scheme.

	a	b
$\lvert F_o \rvert < 7.65$	1.46	−0.13
$7.65 < \lvert F_o \rvert$	0.20	0.03

observed by the criterion $I > 2\sigma(I)$. No absorption correction was applied.

Scattering factors for neutral atoms and anomalous dispersion corrections for Co and Cl were taken from International Tables for X-ray Crystallography (1974).

Solution and Refinement

The non-centrosymmetric space group $P2_1$ was chosen from the statistical distribution of intensities. Confirmation was obtained in the course of the structure solution.

The heavy atom was located from the three-dimensional Patterson map. The positions of the remaining non hydrogen atoms were obtained from Fourier synthesis. Mixed full-matrix least-squares refinement with isotropic temperature factors for the C atoms of the methyl groups, and anisotropic for the remaining atoms with unit weights led to R = 0.057.

A difference synthesis calculated with those reflexions with $\sin \theta/\lambda \leqslant 0.5$ Å^{-1} showed all H atoms as the highest peaks of the map. In order to prevent bias on (ΔF) *vs.* (F_o) or $(\sin \theta/\lambda)$, the last steps of the refinement were carried out with weights $w = 1/(a + b\lvert F_o \rvert)^2$, with the coefficients shown in Table I and calculated by PESOS [15].

TABLE II. Atomic Parameters for $C_{10}N_2H_{20}Cl_2Co$. Coordinates and Thermal Parameters as $U_{eq} = (1/3) \cdot \mathrm{sum}(U_{ij} \cdot A_i{}^* \cdot A_j{}^* J A_i \cdot A_j \cdot \cos(A_i, A_j)) \cdot 10^4$.

Atom	x/a	y/b	z/c	U_{eq}
Co	0.13599(10)	0.36957(221)	0.32867(8)	452(3)
Cl1	0.29649(98)	0.19059(218)	0.30440(65)	838(28)
Cl2	0.70253(101)	0.05307(216)	0.68989(67)	776(27)
N1	0.02087(62)	0.37332(300)	0.48720(42)	424(15)
N2	0.83873(60)	0.37291(291)	0.23122(42)	449(15)
C1	0.16625(90)	0.86191(602)	0.54901(64)	529(25)
C2	0.26516(87)	0.88565(326)	0.69048(65)	533(37)
C3	0.25186(99)	0.88007(334)	0.91271(61)	589(29)
C4	0.47413(159)	0.90724(248)	0.95036(102)	901(34)
C5	0.21103(224)	0.74263(289)	0.96113(137)	1017(42)
C6	0.13019(213)	0.97904(285)	0.96303(136)	951(39)
C7	0.86447(104)	0.86684(302)	0.37322(61)	597(25)
C8	0.99032(137)	0.86695(433)	0.27923(91)	929(25)
C9	0.69920(211)	0.96628(287)	0.35594(137)	1026(40)
C10	0.78104(156)	0.73064(248)	0.35089(100)	717(25)

TABLE III. Analytical and Conductivity Data.

Compound	Colour	Elemental analyses (%)[a]			Molar conductivities[b] λ_M (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
$CoCl_2$ (Bz-DAB)	green	53.26(52.46)	4.70(4.37)	7.91(7.65)	27.99
$CoCl_2$ (c-Hex-DAB)	green	47.05(48.00)	6.93(6.85)	7.84(8.00)	15.16
$CoCl_2$ (i-Pr-DAB)	green	34.78(35.50)	6.01(5.92)	9.93(10.37)	24.94
$CoCl_2$ (t-Bu-DAB)	green	40.27(40.27)	7.10(6.76)	9.43(9.40)	20.40
$CoBr_2$ (Bz-DAB)	green	41.95(42.23)	3.64(3.52)	6.70(6.16)	53.42
$CoBr_2$ (c-Hex-DAB)	green	39.49(38.31)	5.18(5.47)	6.66(6.38)	12.57
$CoBr_2$ (i-Pr-DAB)	green	27.31(26.76)	4.89(4.46)	8.42(7.81)	40.43
$CoBr_2$ (t-Bu-DAB)	green	30.15(31.00)	5.18(5.16)	6.98(7.23)	31.70
$CoCl_2$ $(Ph\text{-}DAB)_2$	purple	59.96(61.16)	4.70(4.40)	9.3(10.27)	31.98
$CoBr_2$ $(Ph\text{-}DAB)_2$	purple	52.03(52.94)	3.91(3.78)	8.00(8.82)	35.15

[a] Theoretical values in parentheses. [b] In acetone (10^{-3} *M* solutions).

TABLE IV. Electronic Spectra in the Visible–U.V. Region.[a]

Compound	Absorption max. (cm^{-1}) ϵ (l cm^{-1} mol^{-1}) in parenthesis
$CoCl_2$(Bz-DAB)	14662(171); 15873sh(93); 17099(110)
$CoCl_2$(c-Hex-DAB)	14450(330); 15290sh(177); 16949(87)
$CoCl_2$(i-Pr-DAB)	14451(485); 15337sh(281); 16833(165)
$CoCl_2$(t-Bu-DAB)	14534(374); 15384sh(217); 16920(138)
$CoBr_2$(Bz-DAB)	14368(398); 15823sh(237); 16181(221)
$CoBr_2$(c-Hex-DAB)	14388(490); 14925sh(372); 16129(173)
$CoBr_2$(i-Pr-DAB)	14388(466); 15038sh(347); 16129(162)
$CoBr_2$(t-Bu-DAB)	14409(510); 15040sh(370); 16132(190)
$CoCl_2(Ph\text{-}DAB)_2$	14492(500); 16120(1420); 19230(2085)
$CoBr_2(Ph\text{-}DAB)_2$	14815(430); 15674(447); 19047(2604)

[a] In acetone as solvent (approx. 10^{-3} *M*).

After refinement, with fixed position for H atoms and temperature factors one unit higher than that of the carbon atom to which they were bonded, the final R = 0.047 and $R_w = 0.057$ where $R_w = (\Sigma w\Delta^2 F/\Sigma w|F_o|^2)^{1/2}$.

A final difference synthesis had no electron density >0.48 e Å^{-3}. The final positional parameters are listed in Table II.

Supplementary Data Available

Tables for anisotropic thermal parameters, H atoms coordinates, and observed *vs.* calculated structure factors are available on request from the Editor or the authors.

Results and Discussion

The compounds were obtained by reaction of anhydrous CoX_2 (X = Cl, Br) or $CoX_2(PPh_3)_2$ (X = Cl, Br) with the corresponding α-diimine. Both are good methods for the preparation of this type of compounds. The use of $CoX_2\cdot 6H_2O$ leads to impure compounds. For instance, in the reaction of $CoCl_2\cdot 6H_2O$ with t-Bu-DAB, $Co_2X(OH)_3$ and t-butylammonium chloride could be identified. For this reason the reaction from anhydrous CoX_2 requires the use of dry acetone. The reaction in ethanol does not lead to the desired compounds.

The reactions were carried out in 1:1 and 1:2 (Co:L) molar ratio, giving compounds of 1:1 stoichiometry for L = Bz-DAB, c-Hex-DAB, i-Pr-DAB, and t-Bu-DAB or of 1:2 stoichiometry for L = Ph-DAB.

Table III shows analytical and physical data for the compounds obtained. The molar conductivities of the complexes in acetone correspond to non-electrolytes [16].

The new complexes can be manipulated in air in the solid state without appreciable decomposition, but in solution they decompose slowly even under nitrogen. They are soluble in acetone, chloroform, THF, dichloromethane and benzene, except $CoCl_2$-(c-Hex-DAB), which is only slightly soluble. All are insoluble in diethyl ether, light petroleum ether and hexane, and decompose in water.

The electronic spectra (Table IV) of the tetrahedral complexes are very similar to those of analogous pseudo-tetrahedral Co(II) complexes [8, 9, 11, 12, 14], the bands at 14000–18000 cm^{-1} being assigned to the $^4T_1(P) \leftarrow {}^4A_2(F)$, ($\nu_3$) transition. The splitting of these bands is attributed to the pseudotetrahedral symmetry. The green colour of these complexes probably results from the combination of ν_3 and the charge-transfer band tail. The spectra of the $CoX_2(Ph\text{-}DAB)_2$ compounds are typical of the octahedral Co^{II} complexes [17]. The structured band at 14000–16000 cm^{-1} is assigned to the $^4A_2(F) \leftarrow {}^4T_1$, ($\nu_2$) transition and the splitting is attributed to the pseudo-octahedral symmetry. The band at *ca.* 19000 cm^{-1} is assigned to the $^4T_1 \leftarrow {}^4T_1(\nu_3)$ transition.

The effective magnetic moment of all these complexes (Table V) increases with temperature and the reciprocal magnetic susceptibilities obey the Curie–Weiss law with θ over the range –23 to –60 °K. The magnetic moments of the $CoX_2(Ph\text{-}DAB)_2$ complexes at room temperature fit in the range of Co^{II} octahedral complexes [18]. The CoX_2(R-DAB) complexes have magnetic moments of 3.58–4.77 B.M. at room temperature and some of them seem to be too high with respect to the typical values of tetrahedral Co^{II} complexes [18]; however our magnetic moment values at room temperature are similar to those reported for other Co^{II} α-diimine

TABLE V. Magnetic Susceptibilities and Effective Magnetic Moments at Various Temperatures.

Compound	$10^6\ \chi_M$ (T, K)	$10^6\ \chi'_M$	μ_{eff} (B.M.)	θ (K)
$CoCl_2$(Bz-DAB)	5151(297)	5356	3.58	−50
	7094(206)	7229	3.46	
	9054(151)	9259	3.35	
	14720(77)	14925	3.05	
$CoCl_2$(c-Hex-DAB)	8448(298)	8661	4.56	−35
	11274(206)	11487	4.37	
	15118(151)	15331	4.32	
	25994(77)	26207	4.03	
$CoCl_2$(i-Pr-DAB)	9402(294)	9610	4.77	−60
	12416(206)	12623	4.58	
	15661(151)	15869	4.40	
	25801(77)	26010	4.02	
$CoCl_2$(t-Bu-DAB)	8426(298)	8603	4.54	−29
	11258(206)	11435	4.35	
	15109(151)	15286	4.31	
	26912(77)	27089	4.10	
$CoBr_2$(Bz-DAB)	6516(291)	6741	3.98	−37
	8494(206)	8791	3.81	
	11382(151)	11607	3.76	
	19272(77)	19497	3.48	
$CoBr_2$(c-Hex-DAB)	9336(292)	9575	4.75	−22
	12631(206)	12869	4.62	
	16741(151)	16971	4.55	
	30556(77)	30795	4.37	
$CoBr_2$(i-Pr-DAB)	9198(290)	9425	4.69	−33
	11981(206)	12208	4.50	
	16038(151)	16265	4.45	
	27670(77)	27897	4.16	
$CoBr_2$(t-Bu-DAB)	9342(290)	9620	4.74	−40
	12655(206)	12933	4.63	
	16486(151)	16513	4.48	
	27694(77)	27972	4.17	
$CoCl_2(Ph\text{-}DAB)_2$	8384(298)	8682	4.57	−32
	10974(206)	11272	4.33	
	15049(151)	15346	4.30	
	26746(77)	27043	4.10	
$CoBr_2(Ph\text{-}DAB)_2$	9235(288)	9553	4.71	−28
	12212(206)	12530	4.56	
	16503(151)	16821	4.53	
	28493(77)	28811	4.23	

complexes [8,9,11,12]. The magnetic moment values of the pseudo tetrahedral CoX_2(R-DAB) complexes can be related with the nature of the substituent R present in the R-DAB ligand, the highest μ_{eff} corresponding to the branched cyclohexyl, isopropyl and terbutyl substituents. These substituents can produce a greater distortion from the tetrahedral geometry of the complexes and, consequently, a weaker quenching of the orbital contribution. The magnetic moments of $CoCl_2$(Bz-DAB) are lower than the spin-only value of the Co^{2+} ion, and this could be due to the mixing of a low spin state.

TABLE VI. Characteristic I.R. Bands (cm^{-1}).

Compound	ν(C=N)	ν(Co–X)	ν(Co–N)
$\mathrm{CoCl_2}$(Bz-DAB)	–	347s, 315s	332sh, 325sh
$\mathrm{CoCl_2}$(c-Hex-DAB)	1639m, 1589m	347s, 335s	325sh, 308w
$\mathrm{CoCl_2}$(i-Pr-DAB)	1645m, 1592m	348m, 305s	295sh
$\mathrm{CoCl_2}$(t-Bu-DAB)	1644w, 1590w	348s, 320s	322sh
$\mathrm{CoBr_2}$(Bz-DAB)	–	295m, 258m	317m, 310m
$\mathrm{CoBr_2}$(c-Hex-DAB)	1639m, 1588m	284sh, 272s	318m, 308m
$\mathrm{CoBr_2}$(i-Pr-DAB)	1640m, 1590m	285m, 273s	305w, 295sh
$\mathrm{CoBr_2}$(t-Bu-DAB)	1640w, 1585w	280m, 272s	290sh
$\mathrm{CoCl_2}$(Ph-DAB)$_2$	–	314s, 282m	305sh
$\mathrm{CoBr_2}$(Ph-DAB)$_2$	–	247sh, 236s	305sh

TABLE VII. Bond Lengths (Å) and Angles (°) in $\mathrm{CoCl_2}$(t-Bu-DAB). E.s.ds are in parentheses.

Co–N(1)	2.068(5)	C(1)–C(2)	1.510(14)
Co–N(2)	2.065(4)	C(3)–C(4)	1.526(15)
Co–Cl(1)	2.200(27)	C(3)–C(5)	1.552(42)
Co–Cl(2)	2.228(27)	C(3)–C(6)	1.513(33)
N(1)–C(1)	1.269(9)	C(7)–C(8)	1.506(13)
N(1)–C(7)	1.500(7)	C(7)–C(9)	1.515(31)
N(2)–C(2)	1.256(9)	C(7)–C(10)	1.506(37)
N(2)–C(3)	1.506(8)		
N(1)–Co–N(2)	81.6(2)	N(2)–C(2)–C(1)	117.6(9)
N(1)–Co–Cl(1)	116. (1)	N(2)–C(3)–C(4)	113.7(7)
N(1)–Co–Cl(2)	112. (1)	N(2)–C(3)–C(5)	113.6(7)
N(2)–Co–Cl(1)	116. (1)	N(2)–C(3)–C(6)	106. (1)
N(2)–Co–Cl(2)	114. (1)	C(4)–C(3)–C(5)	110. (2)
Cl(1)–Co–Cl(2)	113.8(5)	C(4)–C(3)–C(6)	115. (2)
C(1)–N(1)–C(7)	122.4(7)	C(5)–C(3)–C(6)	108. (1)
C(1)–N(1)–Co	110.1(5)	N(1)–C(7)–C(8)	114.6(6)
C(7)–N(1)–Co	126.7(4)	N(1)–C(7)–C(9)	106. (1)
C(2)–N(2)–C(3)	121.3(6)	N(1)–C(7)–C(10)	106. (2)
C(2)–N(2)–Co	110.4(4)	C(8)–C(7)–C(9)	119. (2)
C(3)–N(2)–Co	127.7(4)	C(8)–C(7)–C(10)	100. (2)
N(1)–C(1)–C(2)	117. (1)	C(9)–C(7)–C(10)	111. (1)

The I.R. spectra (Table VI) of the $\mathrm{CoX_2}$(R-DAB) and $\mathrm{CoX_2}$(Ph-DAB)$_2$ complexes show in the 400–200 cm^{-1} region two Co–X stretching vibrations in ranges typical of non-associated pseudo tetrahedral and octahedral compounds, respectively. Assignments of the ν(Co–N) stretching frequencies in the range 332–290 cm^{-1} were attempted. The possible presence of induced ligand bands in this spectral region makes these assignments difficult and doubtful. The ν(C=N) stretching bands were clearly observed in the c-Hex-DAB, i-Pr-DAB and t-Bu-DAB complexes being split in two bands with respect to those of the free ligands. This fact was also observed by Crociani *et al.* [19] in IIB metal complexes with t-Bu-DAB. In the Bz-DAB and Ph-DAB complexes the ν(C=N) stretching bands could not be clearly observed because of the phenyl group bands which appear in the same spectral region.

A perspective view of the molecule of $\mathrm{CoCl_2}$(t-Bu-DAB) is presented in Fig. 1 [20], which also defines the atomic numbering scheme used. Table VII shows a list of bond angles and bond lengths together with their standard deviations.

The structure consists of individual molecules of $\mathrm{CoCl_2}$(t-Bu-DAB); the packing of the crystal is determined only by van der Waals interactions.

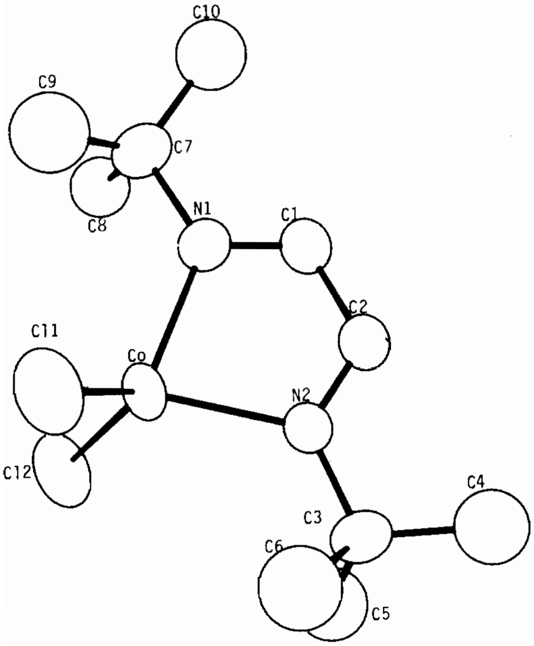

Fig. 1. ORTEP drawing of the molecule. The numbering corresponds to that in Table II.

The Co atom is coordinated to t-Bu-DAB as chelating ligand, and to two Cl atoms, forming a distorted tetrahedron. The lengths Co–N (2.068(5), (2.065(4)) and Co–Cl (2.200(25), (2.228(27)) are as expected for similar complexes [21]. Most of the calculations were carried out with X-RAY 70 [22].

From all these results we can conclude that the nature of the R substituent of the ligands RN=CH–CH=NR exerts an influence on the composition and on the spectral and magnetic properties of the complexes, the steric hindrance being probably the principal factor which determines its behaviour. The phenyl group seems to offer the minimal steric hindrance and the Ph-DAB ligand can form octahedral complexes of CoX$_2$(Ph-DAB)$_2$ composition. The behaviour of the remaining ligands is very similar.

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