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OPTICALLY ACTIVE TRANSITION-METAL COMPOUNDS

XXII *. STEREOCHEMISTRY AND CRYSTAL STRUCTURE DETERMINATION OF $(\eta^5\text{-}C_5H_5)CoI(NC_4H_3\text{-}C(R){=}N(S)\text{-}CH(CH_3)(C_6H_5))$ $(R = H, CH_3)$

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Summary

The crystal structures and absolute configurations of $(\eta^5\text{-}C_5H_5)$-$CoI(NC_4H_3\text{-}C(R){=}N(S)\text{-}CH(CH_3)(C_6H_5))$ ($R = H$, compound I; $R = CH_3$, compound II) have been determined by single crystal X-ray diffraction. Crystals of compound I are orthorhombic, with *a* 11.084(6), *b* 12.107(6) and *c* 13.121(7) Å, space group $P2_12_12_1$ and *d* (calcd, $Z = 4$) 1.69 g cm^{-3}. The structure was solved by the Patterson technique and refined with use of full matrix least-squares methods to $R(F) = 0.031$ and $R_w(F) = 0.028$. Compound II is nearly isomorphous and isostructural; *a* 11.246(6), *b* 11.923(6) and *c* 13.370(7) Å, *d*(calc., $Z = 4$) 1.71 g cm^{-3} and was refined to the final agreement factors of $R(F) = 0.044$ and $R_w(F) = 0.035$. The Co atom has a distorted tetrahedral coordination, with Co–I 2.595(2) for I and 2.607(2) Å for II; Co–(η^5-C_5H_5 ring centroid) 1.681(4) and 1.703(5) Å; Co–N(pyrrole) 1.905(9) and 1.885(9) Å; Co–N(imine) 1.971(8) and 2.003(9) Å, all the parameters being well within values found in the literature. The configuration around the chiral carbon of the phenylethylamine is *S* for both compounds, whereas the configuration around the metal is *R* in I and *S* in II. The different metal configurations in I and II have their origin in the two different substituents ($R = H$, CH_3) at the imine carbon atoms of the chelate ring, which induce completely different conformations of the (S)-$CH(CH_3)(C_6H_5)$ moiety in the two complexes. For both compounds the thermodynamically less stable isomer is enriched upon crystallization. Also, for compound I the solution and solid state conformations are almost opposite to each other, the conformation in the solid reflecting intramolecular interactions (phenyl/C_5H_5 attraction).

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* For parts XXI and XX see ref. 1, 2.

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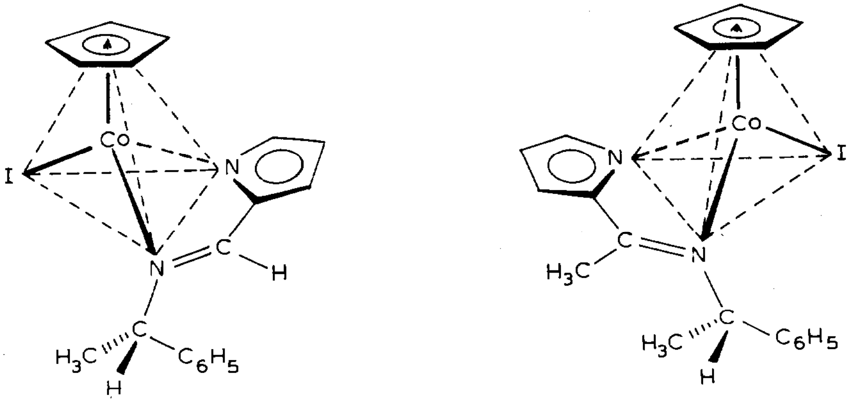
Introduction

From the reaction of $C_5H_5Co(CO)I_2$ with the Schiff bases NN*, derived from 2-pyridine-carbaldehyde, 2-acetylpyridine, 2-benzoylpyridine, 2-pyrrolecarbaldehyde, 2-acetylpyrrole, (−)-1-phenylethylamine and (−)-3-aminomethylpinane, a large number of new complexes has been prepared and characterized [3]. The complexes derived from pyridine Schiff bases NN* are salts $[C_5H_5Co(NN^*)I]^+X^-$, with X = I, PF_6 as counterions, whereas the complexes derived from pyrrole Schiff bases NN* are neutral molecules $C_5H_5Co(NN^*)I$ because the chelate ligands NN* are incorporated as anions obtained by deprotonation at the pyrrole nitrogen.

During the reaction of $C_5H_5Co(CO)I_2$ with Schiff bases NN* a new center of chirality is formed [4] at the Co atom. Using optically pure Schiff bases, the new complexes consist of pairs of diastereomers differing only in the metal configuration. The diastereoisomers in all cases exhibit different ^1H NMR spectra, the integration of which easily gives the diastereoisomer ratio [4].

All the new complexes $[C_5H_5Co(NN^*)I]X$ and $C_5H_5Co(NN^*)I$ proved to have a labile Co configuration. They give equilibrium mixtures of diastereoisomers on dissolution [5] ranging from 99/1 to 61/9 [3]. The assignment as to which is the thermodynamically more stable and less stable diastereomer was made for each pair on the basis of a conformational analysis taking into account intramolecular attractions and repulsions and their effect on the diastereomer ratio at equilibrium, anisotropy effects on chemical shifts, CD spectra, and especially the NOE difference spectra.

The two pyrrole derivatives I and II differing only in the substituent R = H, CH_3 at the imino carbon of the chelate ring (Scheme 1) gave black crystals which could be used for X-ray structure analysis, when solutions in CH_2Cl_2/ether 1/3 were cooled to 243 K [3]. The main goal of the present X-ray structure analyses was the determination of the solid state conformations of molecules I and II and the comparison with the known solution conformations [3].



(I) (II)

SCHEME 1

Experimental

Intensity measurements were carried out on an Enraf-Nonius CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing for both compounds is given in Table 1. Instrumental and procedural details were identical to those described in detail elsewhere [6], and will thus not be repeated here. Data decoding was accomplished using a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factor amplitudes, $|F_0|$. No corrections for absorption were made. All data processing and calculations were carried out using the SHELX-76 [7] system of programs. The structure of compound I was solved by the Patterson technique which gave the position of the iodine atom. All the remaining non-hydrogen atoms, as well as the hydrogens of the pyrrole ring and H(6) of the asymmetric carbon, were found from successive difference Fourier maps. Since there was no reason to expect any distortions in the geometry of the phenyl ring, it was refined as rigid body (with C–C 1.395 Å and idealized hydrogens at C–H 1.00 Å). The C_5H_5 ring was treated in a similar manner. The hydrogens belonging to the phenyl, C_5H_5, methyl and pyrrole groups were refined using a single, isotropic, temperature factor for each unit. Full-matrix least-squares refinement (anisotropic for the non-hydrogen atoms except for the phenyl and C_5H_5 carbons) lead to convergence to the agreement factors listed in Table 1.

Since compounds I and II are essentially isomorphous (the slightly longer cell constants observed for II and the corresponding increase of about 30 Å^3 in the volume of the unit cell being due to the presence of an additional methyl group) the

TABLE 1

SUMMARY OF DATA COLLECTION AND PROCESSING PARAMETERS

	Compound I		Compound II
Space group		$P2_12_12_1$	
Cell constants: a (Å)	11.084(6)		11.246(6)
b (Å)	12.107(6)		11.923(6)
c (Å)	13.121(7)		13.370(7)
Cell volume (Å^3)	1760.8		1792.7
Molecular formula	$C_{18}N_2CoIH_{18}$		$C_{19}N_2CoIH_{20}$
Molecular weight	448.2		462.2
Density (calc.; $Z = 4$) (g cm^{-3})	1.69		1.71
Radiation		Mo-K_α (λ 0.71073 Å)	
Absorption coefficient (cm^{-1})	25.63		25.18
Data collection range		$4° \leq 2\theta \leq 60°$	
Scan width		$\Delta\theta = (1.00 + 0.35 \tan\theta)°$	
Maximum scan time		180	
Scan speed range		0.5–3.35° min^{-1}	
Total data collected	2902		2961
Data with $I > 3\sigma(I)$	1059		1198
Total variables	128		132
$R = \Sigma\vert\vert F_0\vert - \vert F_c\vert\vert / F_0\vert$	0.031		0.044
$R_w = [\Sigma w^2(\vert F_0\vert - \vert F_c\vert)^2/\Sigma w^2\vert F_0\vert^2]^{1/2}$	0.028		0.035
Weights		$w = \sigma(F_0)^{-2}$	
Goodness of fit	0.73		1.76

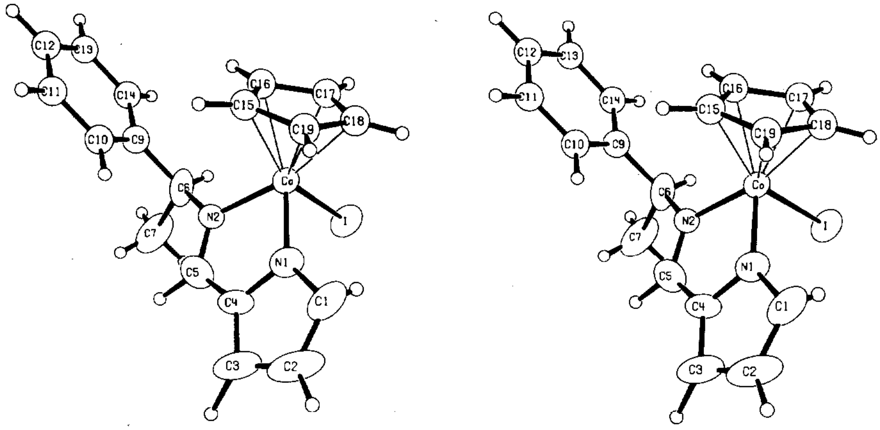


Fig. 1. Stereoscopic view of compound I showing the atomic labelling scheme. The thermal ellipsoids are 50% equiprobability envelopes with hydrogens of arbitrary size.

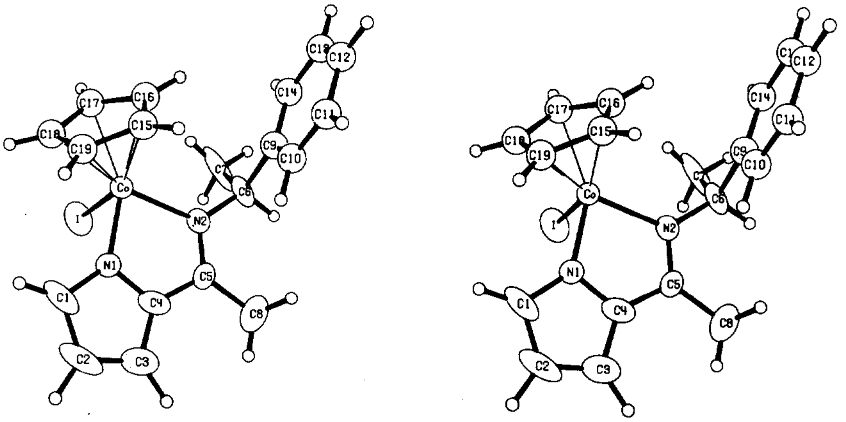


Fig. 2. Stereoscopic view of compound II.

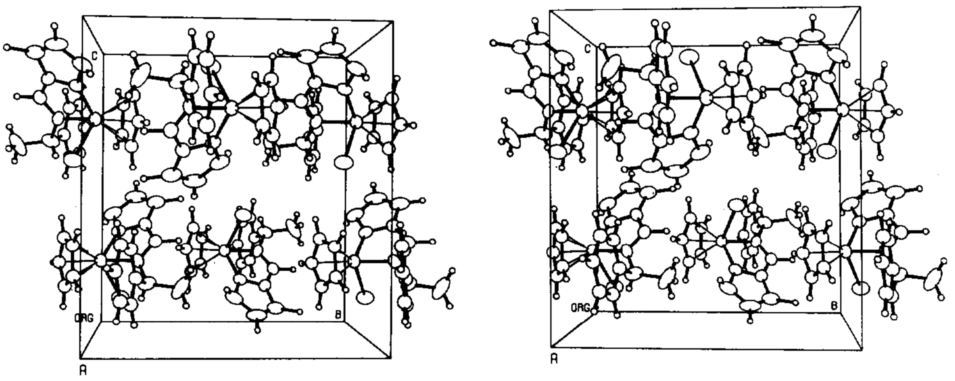


Fig. 3. Stereoscopic view of the molecular packing in the unit cell (compound I).

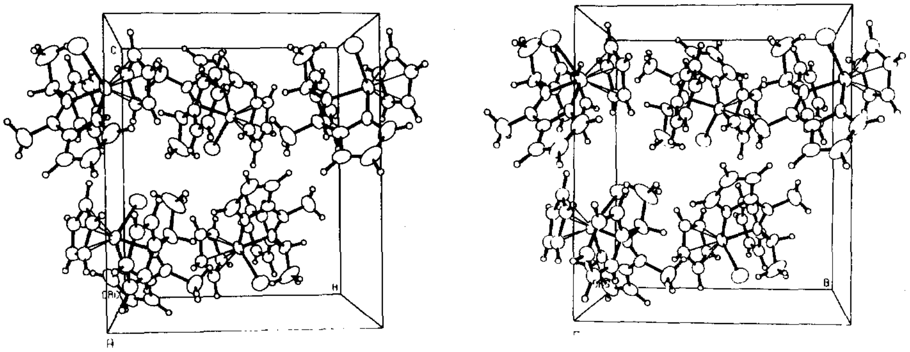


Fig. 4. Stereoscopic view of the molecular packing for compound II.

final coordinates of the iodine and cobalt atoms of compound I were used in the initial stages of the refinement of complex II. All the subsequent details of refinement were similar to those used for the first compound. Bond lengths, angles, and least-squares planes are listed in Tables 3–5 *. The atomic labelling scheme (which is identical for both compounds, except for that of the additional methyl group present in compound II, C(8)) is shown in Figs. 1 and 2. The labelling scheme of the hydrogens is such that their numbers are identical to those of the carbons they are attached to. Packing diagrams for both compounds are presented in Figs. 3 and 4. The stereo-drawings were obtained by using Johnson's ORTEP 2 [8].

Determination of the absolute configuration

The absolute configuration of the two compounds was determined by the Bijvoet method [9]. For both compounds, twelve reflections showed marked differences between $F_c(hkl)$ and $F_c(\overline{hkl})$ (Table 6). These reflections were measured and the results clearly show that the coordinates initially chosen for compound I correspond to those of the correct enantiomer, whereas those of compound II correspond to the wrong enantiomer. Both structures were then refined in their correct absolute configurations to the final agreement factors listed in Table 1. The coordinates given in Table 2 are those of the correct enantiomer. The absolute configurations of the molecules are shown correctly in Figs. 1 and 2, as well as in the packing diagrams.

Applying the extension of the *R*, *S* system [10] to polyhapto ligands in organometallic complexes [4,11,12], the priority sequence of the ligands at the cobalt atom is $I > (\eta^5\text{-}C_5H_5) > \text{N(imine)} > \text{N(pyrrole)}$. Consequently, the configuration around the metal atom is *R* for compound I and *S* for II. An internal check on these results is that the Bijvoet test correctly predicts that the configuration around C(6), the chiral carbon derived from the optically active amine ligand, is *S* (the priority sequence of the ligands around C(6) being N(imine) > C(phenyl) > C(methyl) > H), a fact unknown to the crystallographers prior to absolute configuration determination.

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* Tables of thermal parameters and structure factors are available from the authors.

TABLE 2

ATOMIC COORDINATES FOR COMPOUNDS I AND II

Atom	x/a	y/b	z/c
Compound I			
I	0.45709(8)	−0.07790(8)	0.59567(6)
Co	0.3166(1)	−0.0085(1)	0.7403(1)
N(1)	0.4125(8)	−0.0703(10)	0.8464(6)
N(2)	0.2400(8)	−0.1554(7)	0.7448(8)
C(1)	0.5110(11)	−0.0412(13)	0.9091(11)
C(2)	0.5359(15)	−0.1338(15)	0.9721(10)
C(3)	0.4545(14)	−0.2173(12)	0.9521(10)
C(4)	0.3820(12)	−0.1779(12)	0.8717(9)
C(5)	0.2857(13)	−0.2198(12)	0.8129(10)
C(6)	0.1486(12)	−0.1936(13)	0.6705(10)
C(7)	0.1527(11)	−0.3204(11)	0.6551(10)
C(9)	0.0218(4)	−0.1554(3)	0.6985(5)
C(10)	−0.0160(4)	−0.1386(3)	0.7987(5)
C(11)	−0.1349(4)	−0.1076(3)	0.8187(5)
C(12)	−0.2160(4)	−0.0933(3)	0.7384(5)
C(13)	−0.1781(4)	−0.1102(3)	0.6382(5)
C(14)	−0.0592(4)	−0.1412(3)	0.6183(5)
C(15)	0.1795(4)	0.0897(3)	0.8017(5)
C(16)	0.1685(4)	0.0853(3)	0.6940(5)
C(17)	0.2770(4)	0.1267(3)	0.6511(5)
C(18)	0.3551(4)	0.1567(3)	0.7322(5)
C(19)	0.2949(4)	0.1338(3)	0.8254(5)
H(1)	0.5409(53)	0.9897(63)	0.8757(54)
H(2)	0.5851(61)	0.8671(58)	0.0222(49)
H(3)	0.4703(60)	0.6827(57)	0.9625(50)
H(5)	0.2596(73)	−0.3107(75)	0.8180(62)
H(6)	0.1760(82)	−0.1700(81)	0.6171(68)
H(7A)	0.1264(11)	−0.3579(11)	0.7193(10)
H(7B)	0.2369(11)	−0.3436(11)	0.6380(10)
H(7C)	0.0973(11)	−0.3414(11)	0.5982(10)
H(10)	0.0421(4)	−0.1488(3)	0.8563(5)
H(11)	−0.1621(4)	−0.0955(3)	0.8905(5)
H(12)	−0.3012(4)	−0.0711(3)	0.7527(5)
H(13)	−0.2362(4)	−0.1000(3)	0.5806(5)
H(14)	−0.0321(4)	−0.1532(3)	0.5464(5)
H(15)	0.1170(4)	0.0659(3)	0.8522(5)
H(16)	0.0969(4)	0.0578(3)	0.6552(5)
H(17)	0.2952(4)	0.1335(3)	0.5767(5)
H(18)	0.4380(4)	0.1884(3)	0.7251(5)
H(19)	0.3279(4)	0.1466(3)	0.8953(5)
Compound II			
I	−0.48049(8)	0.09179(9)	−0.59905(8)
Co	−0.3182(1)	0.0099(1)	−0.7176(1)
N(1)	−0.4198(9)	0.0323(9)	−0.8279(7)
N(2)	−0.2563(8)	0.1611(8)	−0.7574(8)
C(1)	−0.5104(12)	−0.0243(13)	−0.8736(11)
C(2)	−0.5519(12)	0.0451(16)	−0.9501(13)
C(3)	−0.4861(14)	0.1420(13)	−0.9515(10)
C(4)	−0.4053(11)	0.1330(13)	−0.8737(9)
C(5)	−0.3128(11)	0.2035(11)	−0.8332(10)
C(6)	−0.1624(10)	0.2281(11)	−0.7062(10)

TABLE 2 (continued)

Atom	x/a	y/b	z/c
C(7)	−0.1897(10)	0.2408(12)	−0.5991(12)
C(8)	−0.2928(12)	0.3173(11)	−0.8782(12)
C(9)	−0.0405(5)	0.1732(3)	−0.7269(5)
C(10)	−0.0155(5)	0.1357(3)	−0.8235(5)
C(11)	0.0958(5)	0.0903(3)	−0.8454(5)
C(12)	0.1821(5)	0.0825(3)	−0.7707(5)
C(13)	0.1571(5)	0.1200(3)	−0.6742(5)
C(14)	0.0457(5)	0.1653(3)	−0.6523(5)
C(15)	−0.1768(5)	−0.0963(3)	−0.7615(5)
C(16)	−0.1598(5)	−0.0622(3)	−0.6607(5)
C(17)	−0.2606(5)	−0.0969(3)	−0.6048(5)
C(18)	−0.3398(5)	−0.1526(3)	−0.6709(5)
C(19)	−0.2880(5)	−0.1522(3)	−0.7678(5)
H(1)	0.4572(13)	0.9000(13)	0.1407(13)
H(2)	0.3793(13)	0.0272(13)	0.9998(13)
H(3)	0.5019(13)	0.2116(13)	0.0003(13)
H(6)	0.8462(12)	0.3197(12)	0.2763(12)
H(7A)	−0.1263(10)	0.2863(12)	−0.5657(12)
H(7B)	−0.1935(10)	0.1648(12)	−0.5677(12)
H(7C)	−0.2682(10)	0.2793(12)	−0.5911(12)
H(8A)	−0.3478(12)	0.3290(11)	−0.9361(12)
H(8B)	−0.2086(12)	0.3229(11)	−0.9017(12)
H(8C)	−0.3081(12)	0.3760(11)	−0.8263(12)
H(10)	−0.0773(5)	0.1413(3)	−0.8770(5)
H(11)	0.1138(5)	0.0635(3)	−0.9146(5)
H(12)	0.2619(5)	0.0499(3)	−0.7865(5)
H(13)	0.2189(5)	0.1143(3)	−0.6207(5)
H(14)	0.0278(5)	0.1922(3)	−0.5830(5)
H(15)	−0.1203(5)	−0.0833(3)	−0.8181(5)
H(16)	−0.0893(5)	−0.0209(3)	−0.6339(5)
H(17)	−0.2735(5)	−0.0845(3)	−0.5316(5)
H(18)	−0.4183(5)	−0.1862(3)	−0.6525(5)
H(19)	−0.3236(5)	−0.1854(3)	−0.8295(5)

Results and discussion

As shown in Figs. 1 and 2, the molecules of compounds I and II consist of a central cobalt atom surrounded by iodine, two nitrogen atoms and a $(\eta^5\text{-C}_5\text{H}_5)$ group.

On the assumption that the $(\eta^5\text{-C}_5\text{H}_5)$ ligand can be counted as a single binding point to the metal, the coordination polyhedron around the Co atom can be described as a distorted tetrahedron. This type of coordination was proposed by Haymore et al. [13] for the somewhat related compound $\text{CoI(NO)}_2\text{P(C}_6\text{H}_5)_3$. However, in view of the large deviations of the angles around the central atom observed for compounds I and II (the values ranging from 82.2(4) to 130.7(1)°), the tetrahedral geometry is only an approximate representation. It is generally assumed that this distorted geometry can be considered as being derived from an octahedral arrangement obtained by the collapse of three facial points [14]. Thus, the three angles associated with N(1), N(2) and I are all relatively close to 90°. The biggest

TABLE 3

INTRAMOLECULAR BOND DISTANCES (Å)

	Compound I	Compound II
Co–I	2.595(2)	2.607(2)
Co–N(1)	1.905(9)	1.885(9)
Co–N(2)	1.971(8)	2.003(9)
Co–C(15)	2.091(4)	2.116(5)
Co–C(16)	2.086(5)	2.119(5)
Co–C(17)	2.059(5)	2.079(6)
Co–C(18)	2.047(3)	2.050(4)
Co–C(19)	2.067(4)	2.074(4)
Co–Cent [a]	1.681(4)	1.703(5)
N(1)–C(1)	1.41(1)	1.37(1)
C(1)–C(2)	1.42(2)	1.40(2)
C(2)–C(3)	1.38(2)	1.37(2)
C(3)–C(4)	1.41(1)	1.39(2)
N(1)–C(4)	1.39(1)	1.36(1)
C(4)–C(5)	1.41(1)	1.44(2)
C(5)–C(8)	–	1.50(1)
C(5)–N(2)	1.29(1)	1.30(1)
N(2)–C(6)	1.48(1)	1.49(1)
C(6)–C(7)	1.55(2)	1.47(2)
C(6)–C(9)	1.52(1)	1.54(1)

[a] Cent: centroid of (η^5-C_5H_5) ring.

TABLE 4

INTRAMOLECULAR BOND ANGLES (°)

	Compound I	Compound II
Cent–Co–I	122.9(1)	122.8(1)
Cent–Co–N(1)	125.6(1)	124.4(1)
Cent–Co–N(2)	130.5(1)	130.7(1)
N(1)–Co–I	94.1(2)	89.9(3)
N(1)–Co–N(2)	82.2(4)	82.8(4)
N(2)–Co–I	89.3(3)	93.9(3)
Co–N(1)–C(1)	139(1)	137(1)
Co–N(1)–C(4)	114.1(8)	113.9(9)
C(1)–N(1)–C(4)	106(1)	109(1)
N(1)–C(1)–C(2)	107(1)	107(1)
C(1)–C(2)–C(3)	110(1)	109(1)
C(2)–C(3)–C(4)	105(1)	106(1)
N(1)–C(4)–C(3)	111(1)	109(1)
N(1)–C(4)–C(5)	113(1)	116(1)
C(3)–C(4)–C(5)	136(1)	135(1)
N(2)–C(5)–C(4)	117(1)	115(1)
N(2)–C(5)–C(8)	–	126(1)
C(4)–C(5)–C(8)	–	119(1)
Co–N(2)–C(5)	113.4(9)	112.8(8)
Co–N(2)–C(6)	123.9(8)	127.3(8)
C(5)–N(2)–C(6)	122(1)	120(1)
N(2)–C(6)–C(7)	112(1)	111(1)
C(7)–C(6)–C(9)	111.1(9)	114 (1)
N(2)–C(6)–C(9)	112.2(9)	108.6(8)
C(6)–C(9)–C(10)	123.3(5)	118.8(5)
C(6)–C(9)–C(14)	116.7(5)	121.2(5)

deviation from 90° is observed for the N(1)–Co–N(2) angle (82.2(4) and 82.8(4)°), this contraction being the result of the formation of the five-membered chelate ring.

The cobalt–iodine distances (2.595(2) and 2.607(2) Å) observed for compounds I and II, respectively, appear to be normal. Haymore et al. [13] reported a Co–I bond of 2.572(1) Å for the $CoI(NO)_2P(C_6H_5)_3$ complex and a value of 2.545(4) Å was observed for the $CoI(NO)_2P(C_6H_5)_2R$ ($R = CH_2CH_2P(O)(C_6H_5)_2$) compound [15].

The Co–C(Cp) distances range from 2.047(3) to 2.091(4) Å for compound I and from 2.050(4) to 2.119(5) Å for II with averages of 2.070 and 2.088 Å. The two longest Co–C(Cp) distances are those to C(15) and C(16), the carbons closest to the Schiff base. A similar behavior was observed in the related complex of (η^5-C_5H_5)$Mo(CO)_2(C_4H_3NCH{=}NR)$ with $R = (CH)(CH_3)(C_6H_5)$ [16]. The Co–(η^5-C_5H_5 ring centroid) distances of 1.681(4) and 1.703(5) Å are well within the range of values reported in the literature [17].

As in the case of similar Mo complexes [16,18] the two Co–N distances are quite different, the Co–N(pyrrole) bonds being significantly shorter (1.905(9) and 1.885(9)

TABLE 5

LEAST-SQUARES PLANES AND DEVIATIONS OF ATOMS FROM THESE PLANES (Å) (First entry is for compound I, the second for compound II)

(a) Coefficients of $Ax + By + Cz - D = 0$			A	B	C	D
Plane 1: N(1), C(1), C(2), C(3), C(4)			0.6368	−0.3596	−0.6821	−4.349
			0.6553	−0.4179	−0.6292	3.707
N(1)	−0.008	0.003				
C(1)	−0.002	0.002				
C(2)	0.013	−0.006				
C(3)	−0.019	0.008				
C(4)	0.018	−0.007				
Plane 2: Co, N(1), N(2), C(4), C(5)			0.6536	−0.3392	−0.6766	−4.240
			0.6668	−0.4244	−0.6126	3.454
Co	−0.004	−0.013				
N(1)	0.003	0.016				
N(2)	0.005	0.012				
C(4)	−0.005	−0.010				
C(5)	−0.004	−0.005				
Plane 3: C(15), C(16), C(17), C(18), C(19)			−0.3852	0.9228	−0.0015	0.219
			−0.4501	0.8704	−0.1994	−1.925
Plane 3: C(9), C(10), C(11), C(12), C(13), C(14)			0.2614	0.9630	−0.0656	−2.350
			0.3367	0.9101	−0.2416	4.074

(b) Dihedral angles (°)

1/2	2/3	3/4
1.55	124.32	38.00
1.21	123.19	46.46

Å) than the Co–N(imine) bonds (1.971(8) and 2.003(9) Å). The pyrrole ring and the chelate ring are virtually coplanar, the dihedral angles between them being 1.55 and 1.21°. The dihedral angles between the chelate ring and the Cp ligand are 124.32 and 123.19°.

The structural characteristics and differences between compounds I and II can easily be observed in Fig. 5, which represents a double stereo picture drawn using program BMFIT [19]. Since the configurations around the central metal atom are *R* for I and S for II, the coordinates of II had to be inverted, giving *R* configuration at Co and at C(7). The plots were drawn by least-squares fitting of Co, I, pyrrole, the chelate ring and of C(6), the chiral carbon. The double stereo picture clearly shows that, in spite of the change of chirality at the central metal atom, the geometry around it remains essentially unchanged. Thus, the distances between the corresponding common atoms are small and vary from 0.02 Å, observed for the Co atom, to 0.29 Å for the iodine atom. This difference between the two corresponding iodine atoms is reflected in the two Co–I bond lengths (2.595(2) versus 2.607(2) Å). Besides this small elongation of the Co–I bond in II relative to I there is a small opening of the N(2)–Co–I angle from 89.3 to 93.9° and of the Co–N(2)–C(6) angle from 123.9 to 127.3° in going from I to II. These small but significant differences are probably

TABLE 6

DETERMINATION OF ABSOLUTE CONFIGURATION FOR COMPOUNDS I AND II

Indices	$F_c(hkl)$	$F_c(\overline{hkl})$	$F_c(hkl)/F_c(\overline{hkl})$	$F_{obs}(hkl)/F_{obs}(\overline{hkl})$
Compound I				
1,2,1	115	109	1.06	1.05
4,2,3	26	30	0.87	0.89
5,1,3	32	34	0.94	0.94
5,8,5	43	41	1.05	1.05
2,8,5	33	35	0.94	0.96
5,7,5	19	21	0.90	0.93
5,3,5	29	27	1.07	1.08
1,2,5	22	20	1.10	1.06
6,6,6	19	21	0.90	0.95
2,8,7	36	38	0.95	0.95
1,5,7	31	33	0.94	0.94
2,2,7	38	40	0.95	0.95
Compound II				
1,4,1	8	10	0.80	1.21
10,1,2	14	12	1.17	0.91
2,4,2	29	31	0.93	1.07
1,8,3	17	19	0.89	1.06
4,3,3	47	44	1.07	0.93
1,3,4	57	54	1.06	0.95
4,4,4	58	61	0.95	1.05
3,7,4	15	17	0.88	1.05
5,9,6	14	16	0.87	1.13
4,1,7	21	19	1.10	0.95
2,4,8	16	18	0.89	1.11
1,6,8	27	30	0.90	1.08

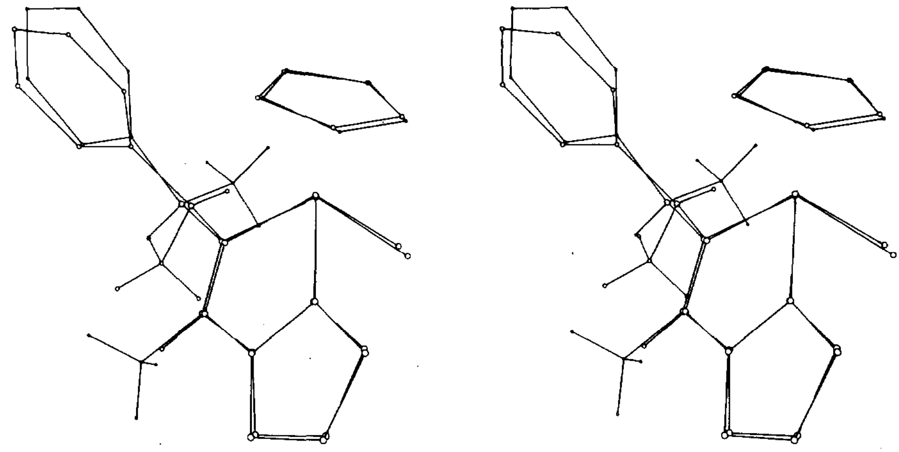


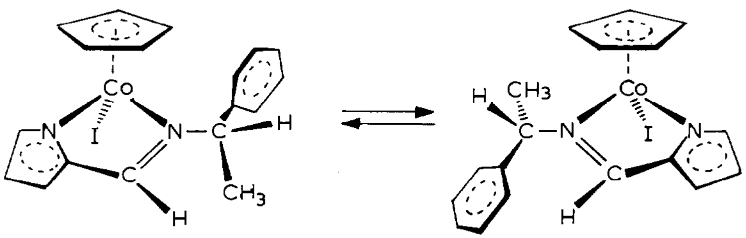
Fig. 5. A double stereo picture of compounds I and II.

due to steric hindrance between iodine and the C(7) methyl group which occurs in compound II (H(7C)–I 3.28 Å; H(7B)–I 3.36 Å). However, in the case of compound I the configuration around the metal is such that H(6) and not the C(7) methyl group points toward the iodine atom. As can clearly be seen from Fig. 5, the biggest differences between the two compounds occur for the phenyl groups where distances as large as 0.8 Å were observed between corresponding carbons. This behavior is exemplified in the differences between the phenyl/C_5H_5 dihedral angles which are 38.00 and 46.46° for compounds I and II, respectively. In both cases the phenyl rings point towards the (η^5-C_5H_5) group assuming the characteristic edge-to-face arrangement observed for a variety of other related complexes [3,20–29].

Solution stereochemistry of I and II

In solution complexes I and II consist of two diastereomers differing only in the Co configuration (*R* and *S*) and having the same ligand configuration (*S*). The diastereomer ratio in $CDCl_3$ solution at room temperature was measured for I as 80/20 and for II as 70/30 [3]. In both cases we did not succeed in diastereomer separation or enrichment by fractional crystallization or chromatography. Solutions obtained from crystalline material, even solutions at 243 K, contained only the equilibrium mixture [3]. Therefore, if there is isomer separation on crystallization there must be a fast change of the metal configuration in solution. This fast isomerization at the Co atom is obvious from the magnetization transfer on saturation of individual signals of the diastereomers *RS* and *SS* of I, due to chemical exchange [3].

The labile Co configuration probably has its origin in the tendency of the Co–I bond to dissociate. The dissociation of an iodine ligand with formation of a configurationally even more labile acetone solvate and iodide attack from the backside would lead to an inversion of the Co configuration in one step and to ultimate epimerization after many steps. Indications for this hypothesis are the easy substitution of I^- by other ligands [3] and the conductivities of solutions of complexes of type I and II which are close to the values of 1 : 1 electrolytes. Thus,



SCHEME 2

complex II in acetone solution at room temperature has a conductivity of 88 cm^2 mol^{-1} Ω^{-1}, indicating extensive ion formation [3].

For complex I, 400 MHz ^1H NMR NOE difference spectra were obtained in acetone solution at 254 K [3]. On this basis, the *S* configuration was assigned to the thermodynamically more stable diastereomer of I (80% of *SS* at equilibrium), the thermodynamically less stable diastereomer being the *RS* form (20% of *RS* at equilibrium). The solution orientations of the $CH(CH_3)(C_6H_5)$ substituent in *RS* and *SS* diastereomers of I, inferred from these NOE experiments are shown in Scheme 2. In the *SS* isomer C*–H and C*–C(phenyl) and in the *RS* isomer C*–H and C*–C(methyl) stagger the C–H bond at the adjacent imine carbon atom; in both cases the hydrogen substituent is between the ligand plane of NN* and η^5-C_5H_5.

The solution structure of compound II has not been studied by the NOE technique. However, the conformational analysis of complexes analogous to II, revealed that for compounds, containing a large substituent $R = CH_3$ (II) or C_6H_5 instead of $R = H$, the assignment of the metal configuration to thermodynamically more stable and less stable diastereomers had to be inverted [3]. Thus, for II the thermodynamically more stable diastereomer in solution has *R* configuration at Co (70% of *RS* at equilibrium) and the thermodynamically less stable diastereomer has *S* configuration at Co (30% of *SS* at equilibrium).

Comparison of solid state and solution stereochemistry

The X-ray structure determination of the crystal of I, shows that it contains the *RS*-isomer which is the thermodynamically less favored isomer in solution. Therefore, it must be assumed that on crystallization the isomer, present in the equilibrium mixture with only 20%, crystallizes first. Due to the labile Co configuration during crystallization at 243 K, a complete transformation to the *RS*-form takes place. Similar arguments also apply to (II) for which the *SS*-isomer (30% at equilibrium mixture) crystallizes first. This behavior, surprising in view of the concentrations, is not without precedent. The same phenomenon was observed when I^- in I was replaced by $P(CH_3)_3$ and $PO(OCH_3)_2$. In both cases the thermodynamically less stable isomers were shown to be enriched on crystallization [3].

More surprising, however, is the fact that for I the solution and solid state conformation are almost opposite to each other. Thus, in the solution conformation of the *RS*-isomer of I (Scheme 2) the $CH(CH_3)(C_6H_5)$ substituent must be rotated by ca. 180° to obtain the conformation found in the X-ray structure analysis (Fig. 1). Such a discrepancy between solution and solid state conformations had not been observed before in comparable compounds [20–29]. In the present case it is tentatively explained in the following way. The conformation found in the solid state is in accord with assumptions on intramolecular attractions/repulsions developed earlier [20,21,25,28,29]. There is nothing wrong with the methyl substituent of C* being in the ligand plane as long as the substituent at the adjacent imine C atom in the chelate ring is the small hydrogen atom. Furthermore, in the conformation found in the X-ray structure analysis the molecule gains the phenyl/C_5H_5 attraction. In solution, however, there must be factors which override these intramolecular effects. Such a factor could be ion association in solution. If in complex I, acetone replaces I^-, a cation $[C_5H_5Co(NN^*)(acetone)]^+$ is formed. This cation could form an ion pair with the I^- anion. It is known that nucleophiles attack complexes of type I between the ligand plane and η^5-C_5H_5 [30,31]. If the iodide were to prefer this site in a contact ion pair, then the small hydrogen substituent at the chiral center pointing in this direction would cause the least steric hindrance and guarantee best ion contact. Effects like this could be the reason why in both solution conformations of (*SS*) and (*RS*) isomers of I the C*–H bonds are located between the ligand plane and η^5-C_5H_5 moiety (Scheme 2).

For II, the conformation found in the solid state is completely in accord with the intramolecular interactions developed earlier [20,21,25,28,29]. For a compound with a methyl substituent at the adjacent imine carbon atom in the chelate ring only the conformation of the optically active group having the C*–H bond in the ligand plane avoids the severe steric hindrance which C*–C(methyl) or C*–C(phenyl) in the ligand plane would cause. As the solution conformation for II has not been determined by NOE spectroscopy, a detailed comparison of solid state and solution conformation is not possible for II.

In conclusion we note that in the case of compounds of type I and II, the conformations found in the solid state reflect the intramolecular interactions; more than a dozen examples show that these interactions are not perturbed by packing forces [20–29]. However, conformations found in solutions may not be indicative of intramolecular forces, because effects such as the one discussed in the present paper may override these interactions.

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