Optically Active Co-ordination Compounds. Part 39.[1] Resolutions and Configurations of Compounds containing the *cis*-Bis(ethylenediamine)-rhodium(III) Moiety

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The *racemic* cations $(\pm)[Rh(en)_2(C_2O_4)]^+$ and $(\pm)[Rh(en)_2(NO_2)_2]^+$ have been resolved, using $(+)[Co(edta)]^-$ as resolving agent. The pair of less-soluble diastereoisomers $(-)[Co(en)_2(C_2O_4)](+)[Co(edta)]$ and $(+)[Rh(en)_2(C_2O_4)](+)[Co(edta)]$ are isomorphous: also isomorphous are $(-)[Co(en)_2(NO_2)_2](+)[Co(edta)]$ and $(+)[Rh(en)_2(NO_2)_2](+)[Co(edta)]$. These isomorphisms define the stereochemistry of these two rhodium cations relative to their cobalt analogues. Since the latter have known absolute stereochemistries, the rhodium compounds may be assigned as D(−). The oxalatorhodium(III) compound as its chloride is shown to undergo spontaneous resolution. By various reactions, chiefly with protonic acids, the resolved oxalato-cation has been converted into optically active $[Rh(en)_2X_2]^+$ ($X = Cl^-$, Br^-, or $[OH]^-$). Chiroptical properties for all the new optically active cations are given.

SINCE the first resolution of a co-ordination compound a constant preoccupation of those interested in the stereochemistry of co-ordination compounds has been to broaden the range of the metal ions involved in dissymmetric co-ordination spheres. This is because the majority of resolved compounds have contained the cobalt(III) ion. Resolutions of compounds of Cr^{III} and such d^6 species as spin-paired Fe^{II}, Rh^{III}, Pt^{IV}, and Ir^{III} are less common but still significant.

We recently extended the range of available optically active co-ordination compounds in two ways. First, we demonstrated [1] the circular dichroism (c.d.) of a number of kinetically labile species, such as trisoxalato-vanadate(III) and -manganate(III). Secondly, in the present work, we have, for the first time, been able to form and examine an extensive series of fairly closely related compounds of Rh^{III}, involving the $4d^6$ electronic configuration, to compare with the much more common cobalt(III) ($3d^6$) case.

Among the compounds of rhodium which have previously been obtained in an optically active form are: some tris(amino-acid) compounds; [2] a few compounds with β-diketonate ligands; [3] and some mixed complexes of ethylenediamine (en) and amino-acids.[4] The present work is based on the bis(ethylenediamine)oxalatorhodium(III) cation,[5] intermediate between the well known tris(ethylenediamine) and tris(oxalato)-species. By utilising the known reactivity towards protonic acids of co-ordinated oxalates, we have also been able to prepare and characterise a number of optically active complex ions of the type $[Rh(en)_2XY]^{n+}$.

RESULTS AND DISCUSSION

The Method of Less-soluble Diastereoisomers.—The resolving agent used was (+)-ethylenediaminetetra-acetatocobaltate(III), $(+)[Co(edta)]^-$. This agent has been used to resolve both $[Cr(en)_2(C_2O_4)]^+$ (ref. 6) and $[Co(en)_2(C_2O_4)]^+$,[7] so there was a very good possibility that it would suffice to resolve $[Rh(en)_2(C_2O_4)]^+$. The easily made L-histidinium salt [8] of $(+)[Co(edta)]^-$ was converted into its potassium salt, which, with the chloride of the *rac*-oxalato-cation $[Rh(en)_2(C_2O_4)]^+$, gave the lavender diastereoisomer $(+)[Rh(en)_2(C_2O_4)](+)[Co(edta)]$ which was recrystallised until optically pure. The c.d. spectrum of the derived optically pure $(+)[Rh(en)_2(C_2O_4)]^+$ ion (two negative bands at 348 and 260 nm) is reported in Table 1. From $K(+)[Co(edta)]$ and the cobalt(III) racemate $[Co(en)_2(C_2O_4)]Cl$, the less-soluble diastereoisomer was $(-)[Co(en)_2(C_2O_4)](+)[Co(edta)]$. The *X*-ray powder results for the two less-soluble diastereoisomers are shown in Table 2. They are clearly isomorphous.

The more-soluble diastereoisomers were not obtained (potassium chloride became the least-soluble species present). However, by using as resolving agent $Ag(+)[Co(edta)]$, then both diastereoisomers could be obtained after the removal of silver chloride. The more-soluble diastereoisomers $(-)[Rh(en)_2(C_2O_4)](+)[Co(edta)]$ and $(+)[Co(en)_2(C_2O_4)](+)[Co(edta)]$ (containing the cations enantiomeric to those discussed above) were obtained 90 and 82% optically pure respectively.

cis-Bis(ethylenediamine)dinitrocobalt(III) ion has been successfully resolved [8] using $[Co(edta)]^-$, the less-soluble diastereoisomer being $(-)[Co(en)_2(NO_2)_2](+)[Co(edta)]$. The dinitrorhodium(III) analogue is certainly closely similar to the cobalt compound and can also be resolved with $[Co(edta)]^-$. The previous method [8] was used on $[Rh(en)_2(NO_2)_2][NO_3]$; the less-soluble diastereoisomer was $(+)[Rh(en)_2(NO_2)_2](+)[Co(edta)]$. The c.d. spectrum of $(+)[Rh(en)_2(NO_2)_2]^+$ is given in Table 1. *X*-Ray powder photographs were taken of the diastereoisomer and compared with those of the cobalt analogue. The results, which demonstrate isomorphism, are given in Table 3.

Resolution of Bis(ethylenediamine)oxalatorhodium(III)

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[1] Part 38, R. D. Gillard, D. J. Shepherd, and D. A. Tarr, *J.C.S. Dalton*, 1976, 594.

[2] J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, 1965, 6531.

[3] J. H. Dunlop, R. D. Gillard, and R. Ugo, *J. Chem. Soc.* (*A*), 1966, 1540.

[4] S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 1968, **7**, 530.

[5] A. W. Addison, R. D. Gillard, P. S. Sheridan, and L. R. H. Tipping, *J.C.S. Dalton*, 1974, 709.

[6] J. H. Vaughan and D. J. Walkwitz, *Inorg. Chem.*, 1966, **5**, 1082.

[7] F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Amer. Chem. Soc.*, 1961, **83**, 1285.

[8] R. D. Gillard, P. R. Mitchell, and C. F. Weick, *J.C.S. Dalton*, 1974, 1635.

Salts by Crystallisation.—The crystals obtained on recrystallising the chemically pure, optically impure, chloride containing 75% (+)[Rh(en)$_2$(C$_2$O$_4$)]$^+$ (*i.e.* 50% optically pure) were now optically pure. This led us to believe that, like[9] [Co(en)$_2$(C$_2$O$_4$)]Cl, the compound [Rh(en)$_2$(C$_2$O$_4$)]Cl could be spontaneously resolved. We did, indeed, obtain optically pure crystals of (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl by adding a solution of (+)[Rh(en)$_2$(C$_2$O$_4$)]$^+$ to a *racemic* solution of [Rh(en)$_2$(C$_2$O$_4$)]Cl.

Werner and Bosshart obtained[10] crystals of (+)[Cr(en)$_2$(C$_2$O$_4$)]Br by adding a crystal of (+)[Co(en)$_2$(C$_2$O$_4$)]Br to a saturated solution of the *racemic* chromium compound. This suggested that the bromides of the two resolved compounds are isomorphs. We similarly obtained crystals of (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl by adding a solution of (−)[Co(en)$_2$(C$_2$O$_4$)]$^+$ to a solution of the *racemic* rhodium compound. Such a small amount of the cobalt compound was used that there was no detectable contamination of the optical isomer of the rhodium compound by the cobalt compound.

TABLE 1

Absorption and c.d. spectra in aqueous solution of *cis*-[Rh(en)$_2$LL′]$^{n+}$ compounds and the cobalt analogues

Compound	Absorption		Circular dichroism		Configuration	Ref.
	a	*b*	*a*	*b*		
(+) [Rh(en)$_2$(C$_2$O$_4$)]$^+$	325	270	348	−2.88	L	*c*
			260	−1.25		
(−) [Co(en)$_2$(C$_2$O$_4$)]$^+$	500	117	520	−2.57	L	*c*
	357	151	386	−0.14		
(+) [Rh(en)$_2$(NO$_2$)$_2$]$^+$	290 (sh)	660	300	−0.8	L	*c*
	245 (sh)	3 500				
(−) [Co(en)$_2$(NO$_2$)$_2$]$^+$	440	224	460	−1.6	L	*c*, 8
			400	+0.65		
	325	380	336	+2.4		
			288	−1.5		
(+) [RhCl$_2$(en)$_2$]$^+$	350	195	400	+0.54	L	*c*
	296	202	307	−0.82		
			236	+1.26		
(+) [CoCl$_2$(en)$_2$]$^+$	620	30	615	−0.6	D	17
	535	69	538	+0.7		
	388	75	420	+0.2		
	318	550	300	−1.1		
			265	+6.0		
(+) [RhBr$_2$(en)$_2$]$^+$			480	−0.17[e]		
	363	260	416	+0.28	L	*c*
			353	−0.47		
	280 (sh)	900	310	−0.15		
			272	+0.85		
(+) [Rh(en)$_2$(OH$_2$)$_2$]$^{3+}$	314	184	314	−0.63	L	*c*
(+) [Co(en)$_2$(OH$_2$)$_2$]$^{3+}$	495	72	480	+1.03	D	*c*, *d*, 17
(+) [Rh(en)$_2$(OH)(OH$_2$)]$^{2+}$	327		320	−0.99	L	*c*
(+) [Co(en)$_2$(OH)(OH$_2$)]$^{2+}$	504	86	494	+1.29	D	*c*, *d*
(+) [Rh(en)$_2$(OH)$_2$]$^+$	330	189	410	+0.03[e]	L	*c*
			335	−0.38		
	276	189	272	−0.29		
(+) [Co(en)$_2$(OH)$_2$]$^{2+}$	518	90	530	+0.79	D	*c*, *d*

[a] Wavelength at peak height. [b] Molar absorption coefficient at peak height. [c] This work. [d] *cf.* R. D. Gillard, *J. Chem. Soc.* (*A*), 1968, 1945. [e] It seems likely that these tiny chiroptical effects (which nevertheless have sizeable *g* factors, because isotropic absorption is so small) correspond to spin-forbidden but magnetic-dipole-allowed transitions.

The basis of such resolution by seeding has been explained[11] using ternary phase diagrams. The essential basis is that the ' seed ' or excess of one enantiomer added to the *racemic* system destroys the mirror symmetry of its ternary diagram, and the first crystals to be obtained will be on that side of the diagram which is now dominant. That is, the crystals will have the same handedness as the seed. The stereochemical configuration of the seeding cation and the cation in the first crystals must be related. That is, from Werner's finding[10] and our own, the related configurations are (+)[Cr(en)$_2$(C$_2$O$_4$)]$^+$, (+)-[Co(en)$_2$(C$_2$O$_4$)]$^+$, and (−)[Rh(en)$_2$(C$_2$O$_4$)]$^+$.

From the relevant phase diagram,[11] one can see that the higher the solubility the readier will be the spontaneous resolution. The perchlorates [M(en)$_2$(C$_2$O$_4$)]-[ClO$_4$] (M = Co, Cr, or Rh) are only slightly soluble in water and the solubility is not very high in boiling water. The negative results obtained on trying to induce crystallisation of optically active material in the presence of perchlorate suggests the formation of a *racemic* compound. Certainly, just as the spontaneously resolving chlorides of [M(en)$_2$(C$_2$O$_4$)]$^+$ are isomorphous, so are the perchlorates (Table 2).

Absolute Configurations of (+)[Rh(en)$_2$(C$_2$O$_4$)]$^+$ *and* (+)[Rh(en)$_2$(NO$_2$)$_2$]$^+$.—The circular dichroism associated with the longest-wavelength absorption band for [M(en)$_2$(C$_2$O$_4$)]$^+$ and *cis*-[M(en)$_2$(NO$_2$)$_2$]$^+$ (M = Rh or Co) is listed in Table 1. The absolute configuration of (−)[Co(en)$_2$(C$_2$O$_4$)]$^+$ (which shows a negative Cotton effect in the region of the lowest-energy spin-allowed *d–d* band) is known to be L since it is the sole product of stereoretentive oxidation (without fission of Co–O bonds)

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[9] K. Yamasaki, H. Igarishi, and Y. Yoshikawa, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 491 and refs. therein.

[10] A. Werner and J. Bosshart, *Chem. Ber.*, 1914, **47**, 2171.

[11] R. M. Secor, *Chem. Rev.*, 1963, **63**, 297 and refs. therein.

of L-$[\mathrm{(en)_2Co_L\{(+)tartrate\}Co_L(en)_2}]^{2+}$: both cobalt ions in this isomer are known [12] from diffraction work to have the L configuration. Since the less-soluble diastereoisomer $(-)[\mathrm{Co(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]$ is isomorphous with $(+)[\mathrm{Rh(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]$ (Table 3) it is clear that $(+)[\mathrm{Rh(en)_2(C_2O_4)}]^+$ has the L configuration. The results on seeding confirm this. From the *X*-ray powder results of Table 2, $(+)[\mathrm{Rh(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$ and $(-)[\mathrm{Co(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$ are isomorphous. The ion $(-)[\mathrm{Co(en)_2(NO_2)_2}]^+$ is known [13] to have the L configuration; therefore $(+)[\mathrm{Rh(en)_2(NO_2)_2}]^+$ has the L configuration.

TABLE 2

X-Ray powder results [*d* spacings (Å) and relative intensities] for $(+)[\mathrm{Rh(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]\cdot\mathrm{H_2O}$, $(-)[\mathrm{Co(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]\cdot 2\mathrm{H_2O}$, $(+)[\mathrm{Rh(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$, and $(-)[\mathrm{Co(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$ (Debye–Scherrer method)

$(+)[\mathrm{Rh(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]\cdot\mathrm{H_2O}$		$(-)[\mathrm{Co(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]\cdot 2\mathrm{H_2O}$		$(+)[\mathrm{Rh(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$		$(-)[\mathrm{Co(en)_2(NO_2)_2}]$ $(+)[\mathrm{Co(edta)}]$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
8.84	s	8.84	vs	4.04	m	4.04	m
7.50	s	7.63	s	3.43	vs	3.43	vs
6.24	m	6.24	m	3.25	vs	3.18	m
5.61	m	5.68	m	2.97	vs	2.97	vs
5.22	vs	5.22	vs	2.64	vs	2.64	vs
4.77	w	4.77	w	2.34	m	2.37	m
4.27	w	4.31	w	2.26	vw	2.29	vw
3.76	m	3.87	vw	2.15	w	2.15	w
2.54	w	2.54	w				
2.22	w	2.20	w				

s = Strong, m = medium, and w = weak.

TABLE 3

X-Ray powder results [*d* spacings (Å) and intensities] for $(+)[\mathrm{Rh(en)_2(C_2O_4)}]\mathrm{Cl}$ {*cf.* $(-)[\mathrm{Co(en)_2(C_2O_4)}]\mathrm{Cl}$} and for $(\pm)[\mathrm{Rh(en)_2(C_2O_4)}][\mathrm{ClO_4}]\cdot 0.5\mathrm{H_2O}$ {*cf.* $(\pm)[\mathrm{Co(en)_2(C_2O_4)}][\mathrm{ClO_4}]\cdot 0.5\mathrm{H_2O}$} (spectrometric method)

$(+)[\mathrm{Rh(en)_2(C_2O_4)}]\mathrm{Cl}$		$(-)[\mathrm{Co(en)_2(C_2O_4)}]\mathrm{Cl}$		$(\pm)[\mathrm{Rh(en)_2(C_2O_4)}][\mathrm{ClO_4}]\cdot 0.5\mathrm{H_2O}$		$(\pm)[\mathrm{Co(en)_2(C_2O_4)}][\mathrm{ClO_4}]\cdot 0.5\mathrm{H_2O}$	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.74	4	3.90	31				
3.33	12	3.28	100	3.28	35	3.25	3
				3.12	9		
				3.06	10		
				3.00	12		
2.92	6	2.90	43	2.85	77	2.88	16
				2.73	7		
2.52	6	2.51	36	2.42	100	2.43	8
				2.38	76		
				2.33	20	2.33	100
2.24	100	2.21	72				
2.12	12	2.10	42	2.13	10	2.13	4

The ion $(+)[\mathrm{Co(en)_2(C_2O_4)}]^+$ is very similar to $(+)[\mathrm{Co(en)_2(CO_3)}]^+$. The chlorides of both compounds are very soluble and the perchlorates are relatively insoluble. In view of the great similarity of the electronic spectra and chiroptical curves for the two compounds, the relative configurations are almost certainly the same (D). However, one could not relate the two compounds by comparing the less-soluble diastereoisomers $(+)[\mathrm{Co(en)_2(C_2O_4)}](+)[\mathrm{Co(en)_2(C_2O_4)_2}]$ and $(+)[\mathrm{Co(en)_2(CO_3)}](+)[\mathrm{Co(en)_2(C_2O_4)_2}]$ since the salts of $(+)[\mathrm{Co(en)_2(C_2O_4)}]^+$ and $(+)[\mathrm{Co(en)_2(CO_3)}]^+$ are not isomorphous. Only a *racemic* mixture of $[\mathrm{Rh(en)_2(C_2O_4)}]\mathrm{Cl}$ or $[\mathrm{Co(en)_2(C_2O_4)}]\mathrm{Cl}$ was obtained on seeding these solutions with $(+)[\mathrm{Co(en)_2(CO_3)}]\mathrm{Cl}$. Similarly, $(-)[\mathrm{Co(en)_2(C_2O_4)}]^+$ and $(-)[\mathrm{Co(en)_2(NO_2)_2}]^+$ cannot be related by comparing $(-)[\mathrm{Co(en)_2(C_2O_4)}](+)[\mathrm{Co(edta)}]$ and $(-)[\mathrm{Co(en)_2(NO_2)_2}](+)[\mathrm{Co(edta)}]$.

The two isomorphous enantiomers $(-)[\mathrm{Co(en)_2(C_2O_4)}]^+$ and $(+)[\mathrm{Rh(en)_2(C_2O_4)}]^+$ {or $(+)[\mathrm{Co(en)_2(C_2O_4)}]^+$ and $(-)[\mathrm{Rh(en)_2(C_2O_4)}]^+$} have very large negative (or positive) Cotton effects and have almost identical rotational strengths. The c.d. spectra of $(+)[\mathrm{Rh(en)_2(C_2O_4)}]^+$ and $(-)[\mathrm{Co(en)_2(C_2O_4)}]^+$ are, allowing for the difference in energies of the long-wavelength absorptions, remarkably similar. For all the bis- and tris-diamine compounds of $\mathrm{Rh^{III}}$ so far studied the L enantiomers have $\alpha_m(589)$ positive,* while rotations for L isomers of $\mathrm{Co^{III}}$ at the sodium lines are usually negative. This arises from the fact that the ligand-field contribution to the optical rotatory dispersion (o.r.d.) curve for the compounds of rhodium has almost vanished at the low-energy sodium D line and the observed rotation $\alpha_m(589)$ is due almost entirely to the massive Cotton effects in the o.r.d. curves of the charge-transfer bands which are positive for the L enantiomers. However, the ligand-field contribution to the rotation of the cobalt enantiomers is significant in the region of the sodium D lines.

Chemical Reactions of Resolved Species.—A number of reactions of co-ordinated oxalato-species have been

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* *Note*: In this paper, the symbol α_m refers to *specific* optical rotations.

[12] R. D. Gillard and M. G. Price, *J. Chem. Soc.* (*A*), **1969**, **1813**.

[13] H. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Japan*, **1972**, **45**, 1755.

noted; typically, for the $[\mathrm{Rh(en)_2(C_2O_4)}]^+$ cation, the addition of hydrohalogenic acids leads[5] to the formation of *cis*-dihalogeno-complexes. Using these patterns of reactivity established for the *rac*-oxalato-complex, we were able to produce a number of transformations of the optically resolved species. These are now described.

Reaction of L-(+)$[\mathrm{Rh(en)_2(C_2O_4)}]^+$ *with hydrohalogenic acids*. Although $[\mathrm{Co(en)_2(C_2O_4)}]^+$ is rather inert towards attack from hydrohalogenic acids at room temperature, $[\mathrm{Rh(en)_2(C_2O_4)}]^+$ is relatively labile.* The ion L-(+)-$[\mathrm{Rh(en)_2(C_2O_4)}]^+$ reacted with dilute HCl yielding (+)-$[\mathrm{RhCl_2(en)_2}]^+$. The c.d. spectrum of the dichloro-product

$$\text{L-}(+)[\mathrm{Rh(en)_2(C_2O_4)}]^+ + 2\mathrm{HCl} \longrightarrow (+)[\mathrm{RhCl_2(en)_2}]^+ + \mathrm{H_2C_2O_4} \quad (1)$$

is reported in Table 1. This reaction proceeds with complete retention of optical activity since the numerical value (0.54) of the molar circular dichroism ($\Delta\varepsilon$) of the dichloro-product at 400 nm was the same as that obtained[14] for its enantiomer by careful recrystallisation of the less-soluble diastereoisomer (−)$[\mathrm{RhCl_2(en)_2}]$(+)-[bcs] (bcs = α-bromocamphorsulphonate), *i.e.* the (+)-$[\mathrm{RhCl_2(en)_2}]^+$ formed in reaction (1) is optically pure. The ion L-(+)$[\mathrm{Rh(en)_2(C_2O_4)}]^+$ reacted with hydrobromic acid to give (+)$[\mathrm{RhBr_2(en)_2}]^+$, which precipitated as its bromide. Its c.d. and electronic spectra are also in Table 1.

Base hydrolysis of (+)$[\mathrm{RhCl_2(en)_2}]^+$. The rate of the aqueous base hydrolysis of *cis*-$[\mathrm{RhCl_2(en)_2}]^+$ is known[15] to be first order in compound and in hydroxide-ion concentrations. All the chloride ions are released, so although the product was not isolated the overall reaction had been assumed to be (2). We carried out this reaction

$$cis\text{-}[\mathrm{RhCl_2(en)_2}]^+ + 2[\mathrm{OH}]^- \longrightarrow cis\text{-}[\mathrm{Rh(en)_2(OH)_2}]^+ + 2\mathrm{Cl}^- \quad (2)$$

on the enantiomer (+)$[\mathrm{RhCl_2(en)_2}]$Cl; the c.d. and electronic spectra of (+)$[\mathrm{Rh(en)_2(OH)_2}]^+$ are given in Table 1. When hydrogen chloride was bubbled into the solution of product which was then set to reflux for 5 min, the original c.d. spectrum of (+)$[\mathrm{RhCl_2(en)_2}]$Cl was regained, showing the reaction to be reversible and to proceed with complete retention of optical activity.

$$(+)[\mathrm{RhCl_2(en)_2}]^+ + 2[\mathrm{OH}]^- \longrightarrow (+)[\mathrm{Rh(en)_2(OH)_2}]^+ + 2\mathrm{Cl}^- \quad (3)$$

Absolute Configuration of Complex Ions of Type (+)$[\mathrm{Rh(en)_2LL'}]^{n+}$.—The chiroptical properties of (+)-$[\mathrm{Rh(en)_2LL'}]^{n+}$ and $[\mathrm{Co(en)_2LL'}]^{n+}$ are shown in Table 1, for L,L′ = $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $[\mathrm{NO_2}]^-$, $\mathrm{H_2O}$, $[\mathrm{OH}]^-$, and LL′ = $[\mathrm{C_2O_4}]^{2-}$. When L or L′ is unidentate, two c.d. bands are obtained in the region of the lowest-energy absorbance band. If LL′ is bidentate, only one c.d. band is obtained in the longer-wavelength region.

Matsumoto *et al.*[16] studied, using the Bijvoet method, the crystal structure of (+)$[\mathrm{CoCl_2(en)_2}]\mathrm{Cl{\cdot}H_2O}$; the compound had the D configuration in agreement with earlier less rigorous chemical work.[17] The ions (−)-$[\mathrm{RhCl_2(en)_2}]^+$ and D-(+)$[\mathrm{CoCl_2(en)_2}]^+$ form less-soluble diastereoisomers with the same resolving agent (+)bcs, so although isomorphism of the less-soluble diastereoisomer $[\mathrm{MCl_2(en)_2}]$(+)[bcs]$\cdot x\mathrm{H_2O}$ has not been established, (−)$[\mathrm{RhCl_2(en)_2}]^+$ very probably has the D configuration. Therefore, the product (+)$[\mathrm{RhCl_2(en)_2}]^+$, from the reaction of L-(+)$[\mathrm{Rh(en)_2(C_2O_4)}]^+$ with HCl, has the L-configuration. Other conversions arise by refluxing L-(+)-$[\mathrm{RhCl_2(en)_2}]^+$ for 1 h with sodium nitrite, which yields L-(+)$[\mathrm{Rh(en)_2(NO_2)_2}]^+$. This in turn can be treated with HCl to reform L-(+)$[\mathrm{RhCl_2(en)_2}]^+$ with no loss of optical activity. Similarly, treating either L-(+)$[\mathrm{Rh(en)_2(C_2O_4)}]^+$ or L-(+)$[\mathrm{Rh(en)_2(NO_2)_2}]^+$ with HBr gave (clearly *via* several stages) (+)$[\mathrm{RhBr_2(en)_2}]^+$ and since its long-wavelength transition has a negative c.d., like that of L-(+)$[\mathrm{RhCl_2(en)_2}]^+$, the ion (+)$[\mathrm{RhBr_2(en)_2}]^+$ probably has the L-configuration.

The ion L-(+)$[\mathrm{RhCl_2(en)_2}]^+$ reacted with sodium hydroxide to give (+)$[\mathrm{Rh(en)_2(OH)_2}]^+$ without loss of optical activity, as in (3) above. The configuration of this dihydroxo-ion (which manifests a negative circular dichroism in the longest-wavelength absorption band) may be deduced as follows. Protonation of its hydroxo-groups involves no Rh–O bond breakage, and so (+)-$[\mathrm{Rh(en)_2(OH)(OH_2)}]^{2+}$ and (+)$[\mathrm{Rh(en)_2(OH_2)_2}]^{3+}$ certainly have the same configuration as (+)$[\mathrm{Rh(en)_2(OH)_2}]^+$. Now, (+)$[\mathrm{Rh(en)_2(OH_2)_2}]^{3+}$ on treatment with nitrite ion yields L-(+)$[\mathrm{Rh(en)_2(NO_2)_2}]^+$, of known configuration. It is known[18] that the reaction of nitrite ion with penta-ammineaquarhodium(III) gives, with no Rh–O bond fission, the penta-amminenitrito-species which isomerises to its linkage isomer penta-amminenitrorhodium(III). By assuming that this finding can be applied to other aquarhodium(III) species reacting with nitrite, then the process (+)$[\mathrm{Rh(en)_2(OH_2)_2}]^{3+}$ + 2-$[\mathrm{NO_2}]^-$ ⟶ L-(+)$[\mathrm{Rh(en)_2(NO_2)_2}]^+$ would occur *via* similar substitutions at the co-ordinated oxygen of water and stereoretentive intramolecular isomerisation, leading to the L-configuration for (+)$[\mathrm{Rh(en)_2(OH_2)_2}]^{3+}$ and its conjugate bases. These chemical reactions are summarised in Scheme 1. As has been our past practice,[19] reactions of rigorously known optical mechanism are indicated by a full line, those of less certainly known optical mechanism by a broken line. This practice is now used by other workers.[20]

At this point, some general remarks can be made about the meaning we attach to ‘ rigorously known ’ in describing optical mechanism. Substitutions at octahedral centres are usually taken to be stereoretentive in two senses, geometric and optical. The feeling, based on the

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* A similar order of reactivity toward nitric acid solutions has recently been studied in detail (N. S. Rowan, R. M. Milburn, and T. P. Dasgupta, *Inorg. Chem.*, 1976, **15**, 1474).

[14] S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1962, **1**, 925.

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[16] K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1970, **43**, 3801.

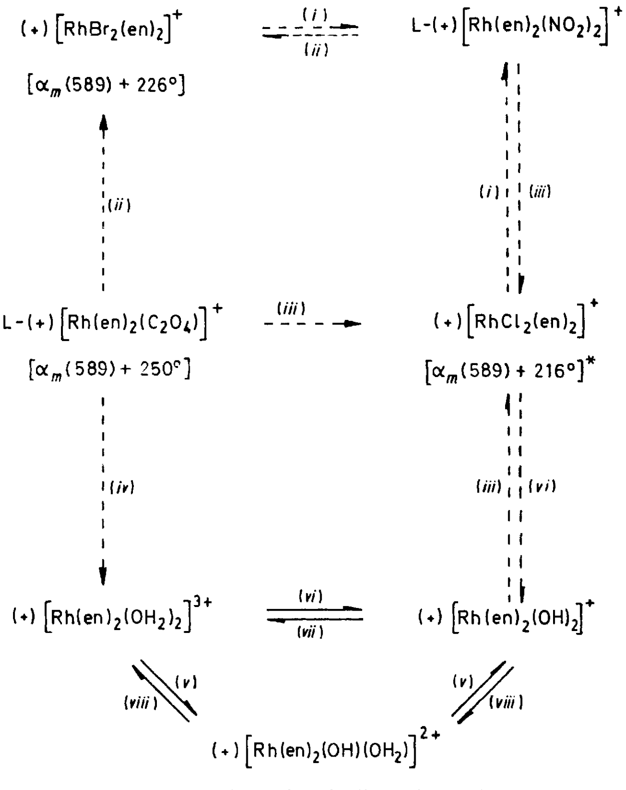
[17] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 1965, 5094.

[18] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.

[19] K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 1965, 6084.

[20] I. J. Kindred and D. A. House, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1359.

retention of optical activity when bonds break at the metal atom, that optical configuration is retained is likely to be true in more cases than not, but it is not necessarily true and it has never been proven rigorously as a generally applicable fact. Statements (very common indeed) based on it are not rigorous, unless supported by detailed evidence. Even where a reaction involving bond breakage at the metal ion from one optically active species to another is fully reversible [*e.g.* for the present base hydrolysis (2) where the value $\alpha_m(589) = +216$ is regained for the dichloro-compound on reversal] the optical mechanism is not rigorously proven in the absence of further information. This is occasionally[20] but not always recognised. To support this caveat, it suffices to catalogue the inversions observed in a number of cases, some total and reversible.[21]



SCHEME 1 Interconversions of optically active cations of the type $[Rh(en)_2XY]^{n+}$. (*i*) $[NO_2]^-$; (*ii*) HBr; (*iii*) HCl; (*iv*) $HClO_4$ (40 °C, 20 mmHg); (*v*) $[OH]^-$; (*vi*) 2 $[OH]^-$; (*vii*) 2 H^+; (*viii*) H^+

* For the opposite isomer, obtained[14] by direct resolution using (+)bcs, $\alpha_m(577.5)$ was reported as −165 °.

Rigorously known optical mechanisms are as follows.[22]

(*i*) Those where no bond breakage occurs at the central metal ion: examples include (*a*) protonations and the reverse, as in $(+)[Co(en)_2(sal)]^+ \longrightarrow (+)[Co(en)_2(Hsal)]^{2+}$ (H_2sal = salicylic acid) {which reaction we use in assigning related configurations to such spectroscopically differing series as $(+)[Rh(en)_2(OH_2)_2]^{3+} \rightleftharpoons (+)[Rh(en)_2(OH)(OH_2)]^{2+} \rightleftharpoons (+)[Rh(en)_2(OH)_2]^+$}; (*b*) $(+)[Co(en)_2(NCS)_2]^+ \longrightarrow (+)[Co(en)_2(NH_3)_2]^{3+}$, and other reactions where the atoms directly attached to the metal ion in the product are throughout the course of the reaction the identical atoms that were attached to it in the reactant; and (*c*) changes of oxidation state at the metal ion, such as $[Ru(phen)_3]^{3+} + e^- \rightleftharpoons [Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline). It is difficult to see the scientific basis for Hawkins' strictures[23] on studies utilising known optical mechanisms.

(*ii*) Those where, although bond breakage (usually substitution) occurs at the metal, the absolute configurations of reactant and product are already known from some independent method, commonly the Bijvoet *X*-ray analysis.

EXPERIMENTAL

Starting Materials and General Methods.—The preparation of the diastereoisomer [L-H_2His][D-Co(edta)]$_2$ was carried out as described in ref. 8, and syntheses of $[M(en)_2(C_2O_4)][ClO_4]\cdot0.5H_2O$ and *cis*-$[M(en)_2(NO_2)_2][NO_3]$ (M = Rh or Co) followed refs. 5, 24, 14, and 25 respectively. Spectroscopic and other instrumental measurements were carried out as described in earlier papers of this series, except that *X*-ray powder methods require some comment.

Results of *X*-ray powder photography (Tables 2 and 3) were recorded for a number of compounds as a means of showing isomorphism and of providing fingerprints. These results were obtained either by the standard Debye–Scherrer method (under the conditions used, with a Buerger-type camera of radius 9 cm, 1-mm linear distance on the film = 1° in θ) or by the spectrometric method[26] where the average number of counts of diffracted *X*-rays was recorded, in our case, at every twentieth of a circular degree in θ. The drawback to the latter, otherwise highly convenient, method is the requirement for large samples (typically, we used 0.5 g). In our Debye–Scherrer photographs, which used nickel-filtered Cu-K_α radiation, both cobalt and rhodium produced rather dense backgrounds (cobalt much the denser), and the precision of the reported *d* spacings and intensities is therefore relatively poor.

Resolutions.—(*a*) $[Rh(en)_2(C_2O_4)]Cl$. (*i*) *With* Ag(+)-[Co(edta)]. The compound $[Rh(en)_2(C_2O_4)][ClO_4]\cdot0.5H_2O$ (1.0 g) was dissolved in boiling water (200 cm^3). The solution was allowed to cool, then passed through an anion-exchange column (Cl^- form). The eluate was concentrated *in vacuo* to 75 cm^3 (solution A). The compound [L-H_2His][D-Co(edta)]$_2$ (1.5 g) was dissolved in the minimum of water and the solution was passed through a cation-exchange column (Ag^+ form). The eluate was concentrated to 25 cm^3 and added to A. The precipitated AgCl was stirred to coagulate it and then removed. The filtrate was concentrated *in vacuo* (25 cm^3) and kept cold overnight. Lavender crystals separated, were collected (reserving the filtrate F for working-up of the other isomer), and dried in air. They were shown to contain $[Rh(en)_2(C_2O_4)]^+$ by passing a solu-

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[21] R. D. Gillard and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 2271.

[22] R. D. Gillard and P. R. Mitchell, *Structure and Bonding*, 1970, **7**, 46.

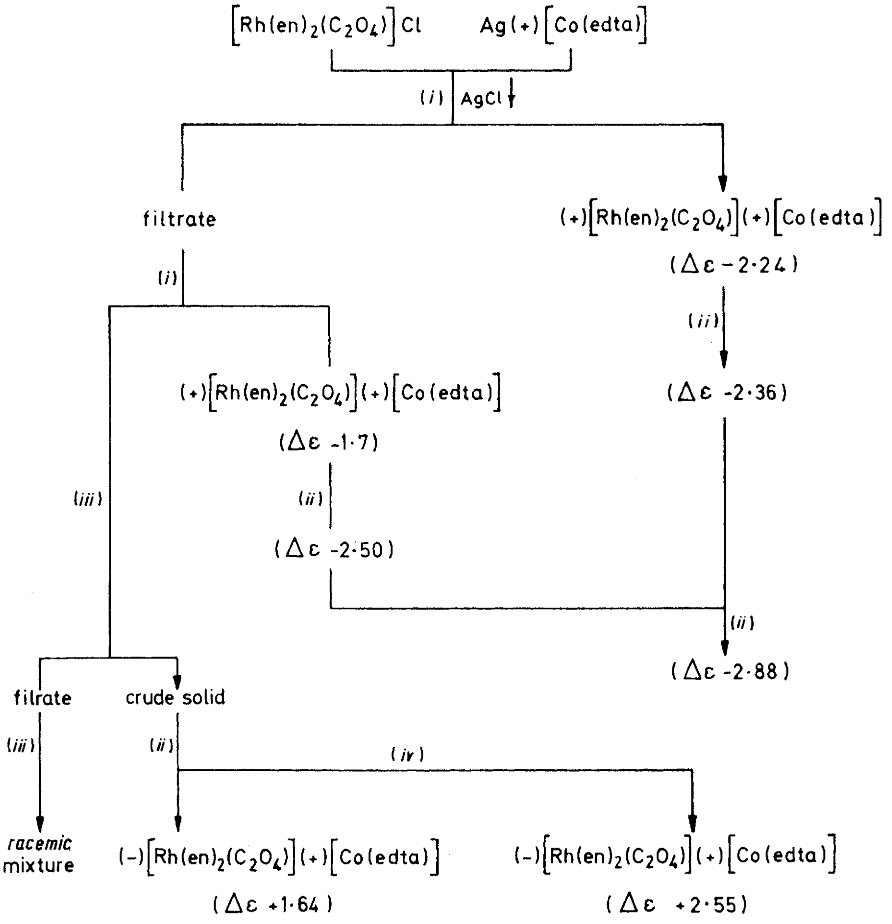
[23] C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley–Interscience, New York, 1971, p. 293.

[24] A. G. Beaumont and R. D. Gillard, *J. Chem. Soc.* (*A*), 1970, 1757.

[25] H. F. Holtzclaw, D. P. Sheetz, and W. D. McCarty, *Inorg. Synth.*, 1953, **4**, 177.

[26] H. P. Klug and L. E. Alexander, '*X*-Ray Diffraction Procedures,' Wiley, New York, 1964, ch. 5.

tion of a few milligrams of the diastereoisomer through an anion-exchange column (Cl^- form) and measuring the electronic spectrum of the cation in the eluant. The eluant was also shown to be optically active; on recrystallising the diastereoisomer, this cationic optical activity increased. This procedure was repeated until there was no further change in optical activity. The filtrate F from the initial crop of the less-soluble diastereoisomer yielded the enantiomeric cation. The steps leading to the purification of both diastereoisomers are summarised in Scheme 2.



SCHEME 2 The values of Δε are for $[Rh(en)_2(C_2O_4)]^+$ at $\lambda_{max.}$ 348 nm. (*i*) Concentrate solution; (*ii*) recrystallise from water; (*iii*) EtOH; (*iv*) filtrate placed in refrigerator

(*ii*) *With* K(+)[Co(edta)]. This method leads to isolation only of the less-soluble diastereoisomer but is quicker. The compound $[Rh(en)_2(C_2O_4)][ClO_4]\cdot 0.5H_2O$ (1.60 g) was dissolved in boiling water (200 cm^3). The solution was allowed to cool, then passed through an anion-exchange column (Cl^- form). The eluate was concentrated to 75 cm^3 *in vacuo* (solution A). The compound $[L\text{-}H_2His][D\text{-}Co(edta)]_2$ (1.5 g) was dissolved in the minimum of water and the solution was passed through a cation-exchange column (K^+ form). The eluate was concentrated to 25 cm^3 and added to A. The resulting solution was evaporated *in vacuo* to 50 cm^3 and cooled overnight in a refrigerator. A mixture of white and lavender crystals formed, were collected, and, after washing with ice-cold aqueous ethanol followed by diethyl ether, were resuspended in water (10 cm^3) at 30 °C and stirred for 15 min. The white crystals redissolved, leaving a few undissolved lavender crystals. At this point the mixture was cooled to −10 °C in an ice–methanol bath. Filtration and washing as before produced 0.3 g of the optically pure diastereoisomer.

(*iii*) *With* $(+)[Rh(en)_2(C_2O_4)]Cl\cdot H_2O$. To an aqueous solution (100 cm^3) of $(\pm)[Rh(en)_2(C_2O_4)]Cl$ (1.0 g) was added $(+)[Rh(en)_2(C_2O_4)]Cl\cdot H_2O$ (10 mg) and the solution was concentrated *in vacuo* until crystallisation was imminent. The solution was kept cold overnight in a refrigerator and the crystals of optically pure $(+)[Rh(en)_2(C_2O_4)]Cl\cdot H_2O$ were collected, washed with methanol, and dried in air (yield 0.3 g).

(*iv*) *With* $(+)[Co(en)_2(C_2O_4)]Cl\cdot H_2O$. The procedure was like that in (*iii*) using $(+)[Co(en)_2(C_2O_4)]Cl\cdot 2H_2O$ (10 mg) instead of the rhodium compound. A similar yield was obtained, but of the enantiomeric laevorotatory compound.

Accurate molar rotations and c.d. were measured for the optically pure enantiomers of $[Rh(en)_2(C_2O_4)]Cl$. Experiments (*iii*) and (*iv*) were repeated using the perchlorates as seeds in place of the chlorides; this resulted in the formation of the solid *racemic* compound.

(*b*) $[Co(en)_2(C_2O_4)]Cl$. (*v*) *With* Ag(+)[Co(edta)]. The method was identical with (*i*) but with $[Co(en)_2(C_2O_4)][ClO_4]\cdot 0.5H_2O$ as the *racemic* material.

(*vi*) *With* K(+)[Co(edta)]. The resolution was carried out as in (*ii*) for the rhodium analogue.

(*vii*) *With* $(-)[Co(en)_2(C_2O_4)]Cl$. The procedure was as in (*iii*) for the rhodium analogue.

(*viii*) *With* (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl. In procedure (*iv*), (+)[Co(en)$_2$(C$_2$O$_4$)]Cl was replaced by (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl.

Experiments (*vii*) and (*viii*) were repeated using the perchlorates instead of the chlorides; again no resolution occurred. The c.d.s of (+)[Co(en)$_2$(C$_2$O$_4$)]Cl and (−)[Co(en)$_2$(C$_2$O$_4$)]Cl were measured to compare with the literature value.

(*c*) *cis*-[Co(en)$_2$(NO$_2$)$_2$][NO$_3$]. This resolution was carried out as recommended.[8]

(*d*) *cis*-[Rh(en)$_2$(NO$_2$)$_2$][NO$_3$]. The same procedure was followed as for the cobalt analogue. Experiments were carried out using as seeds small amounts of nitrates and chlorides of (+)[M(en)$_2$(NO$_2$)$_2$]$^+$ (M = Rh or Co) to try to bring about the spontaneous resolution of (±)[M(en)$_2$(NO$_2$)$_2$]$^+$, but without success.

Reactions of (+)[Rh(en)$_2$(C$_2$O$_4$)]$^+$ *with Concentrated Acids*.—An aqueous solution containing (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl (*ca.* 6 mg) was evaporated to dryness at 30 °C, and to the resulting solid, concentrated HX (X = Cl or Br) (5 cm^3) was added. The solution was kept for 15 min, when the reaction was complete. The residual acid was removed in a few minutes under reduced pressure. The c.d. and molar rotations of the resulting solutions of dihalogeno-complexes were measured.

With HClO$_4$. The volume of an aqueous solution of (+)[Rh(en)$_2$(C$_2$O$_4$)][ClO$_4$], treated with 2 mol dm^{-3} HClO$_4$, was reduced *in vacuo* at 50 °C. The concentrated solution was kept *in vacuo* for several hours until no further change occurred in its electronic spectrum. Absorbance and c.d. spectra were recorded for the final solution. Sodium hydroxide pellets were added to this solution until the pH was greater than 13, and the absorbance and c.d. spectra of the resulting solution were recorded. An identical experiment was performed using (+)[Rh(en)$_2$(C$_2$O$_4$)]Cl·H$_2$O.

Reaction of cis-(+)[RhCl$_2$(en)$_2$]$^+$ *with Sodium Hydroxide*.—A solution of *cis*-(+)[RhCl$_2$(en)$_2$]Cl (10 mg) in 0.1 mol dm^{-3} Na[OH] (5 cm^3) was heated on a steam-bath for 15 min. The resulting solution of *cis*-(+)[Rh(en)$_2$(OH)$_2$]$^+$ was passed through a Sephadex C-25 column (H$^+$ form). Chloride ions were removed from the column by washing with water; sodium ions were eluted with 0.1 mol dm^{-3} nitric acid. The complex cation was presumably converted into *cis*-(+)-[Rh(en)$_2$(OH$_2$)$_2$]$^{3+}$ on the column since 0.75—1.0 mol dm^{-3} HNO$_3$ was needed to elute it. The fractions of the eluant which contained the compound were pooled and freeze-dried overnight to remove HNO$_3$: thermal reaction of HNO$_3$ with the compound was minimal. The solid obtained (a glassy sample of the diaqua-nitrate) was redissolved in water, and electronic and c.d. spectra were obtained. Aliquot portions of Na[OH] (3 mol dm^{-3}) were added, and the pH and c.d. spectra were recorded up to pH 13.

In a second experiment, the original solution from base hydrolysis containing *cis*-(+)[Rh(en)$_2$(OH)$_2$]$^+$ was treated with successive aliquot portions of 0.1 mol dm^{-3} HCl: the c.d. spectra were recorded as a function of pH. Similarly, an aqueous solution (25 cm^3; 10^{-3} mol dm^{-3}) containing *rac*-*cis*-[Rh(en)$_2$(OH$_2$)$_2$]$^{3+}$ was treated with concentrated HCl (5 cm^3) and brought to reflux for 2 min. The electronic spectrum of the final solution showed it to contain rhodium as *cis*-[RhCl$_2$(en)$_2$]$^+$ only. This reaction was very slow at room temperature.

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