Optically Active Co-ordination Compounds. Part XXXII.[1] Potassium (+)Tris-[L-cysteinesulphinato(2−)-*SN*]cobaltate(III): A Versatile Agent for Resolution of 3+ Species

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The yellow anion (+)tris(L-cysu)cobaltate(III) [cysu = cysteinesulphinato(2−)-*SN*], easily obtained in a rapid stereoselective synthesis from L-cysteine, is a very convenient and powerful resolving agent for 3+ cations $[M(L)_3]^{3+}$ [particularly where L = 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy)]. The complexes $[Rh(phen)_3]^{3+}$, $[Rh(bipy)_3]^{3+}$, and $[Rh(phen)_2(NH_3)_2]^{3+}$ have been resolved for the first time and samples of the complexes $[Co(en)_2(phen)]^{3+}$ and $[Co(en)_2(bipy)]^{3+}$ (en = ethylenediamine) obtained with higher optical activities than those previously known.

IT has been said[2] ' A rapid, efficient, and general method for separating optical isomers of co-ordination complexes has long been a goal sought by inorganic chemists. Indeed, Alfred Werner, the founder of co-ordination

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[1] Part XXXI, R. D. Gillard and R. A. Wiggins, *J.C.S. Dalton*, 1973, 125.

[2] L. F. Druding and G. B. Kauffman, *Co-ordination Chem. Rev.*, 1968, **3**, 409.

chemistry, used resolution to establish unequivocally the octahedral configuration for tri-positive cobalt. Often today, a structure proof depends upon proving the existence of optical isomers. Pasteur's classical fractional crystallisation of diastereoisomers which is still the most widely used method of resolution, is tedious and not always reliable.' The last statement needs qualifying, since a number of cases have emerged where resolution is easily achieved by using diastereoisomeric salts of complex ions.

Enantiomers of co-ordination cations were first used as agents for resolving anions by Werner and Basyrin [3] who employed optically active tris(ethylenediamine)cobalt(III) bromide to resolve 2,3-dimethylsuccinic acid.* The first application of complex co-ordination ions as resolving agents for counter-ionic complexes is due to Dwyer who used ions having a similar size and the same, but opposite, charge to the species to be resolved. The soundness of this approach has been discussed by Basolo [5] and the method has been well tested, many resolutions of this kind having been achieved. Thus the use of $(+)[Co(en)_2(NO_2)_2]^+$ (en = ethylenediamine) to resolve 1− species, *e.g.* $[Co(EDTA)]^-$ (ref. 6) and $[Co(en)(ox)_2]^-$ [ox = oxalate(2−)] (ref. 7), and of $(+)[Co(en)_3]^{3+}$ to resolve 3− anions, *e.g.* $[Co(ox)_3]^{3-}$ (ref. 8) and $[Co(CO_3)_3]^{3-}$ (ref. 9), are two examples.

The resolution of certain 3+ species is not a simple procedure because of the lack of a suitable 3− resolving agent, certain optically active species having been obtained only *via* oxidation of the more readily resolved 2+ species.[10] The latter method works well for the ions $[Co(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridyl)[11] and $[Ru(phen)_3]^{3+}$ (phen = 1,10-phenanthroline),[12] where the oxidation states II and III have the same co-ordination number; it is not, of course, practicable for the analogous rhodium(III) complexes where the lower oxidation state, rhodium(I), has a lower co-ordination number.

Schubert [13] investigated an observation made by Michaelis, that when hydrogen peroxide was added to a mixture of cobalt(II) ions and L-cysteine, at pH 7—8 in the presence of air, a bright yellow colour formed due to the formation of tris(L-cysu)cobaltate(III) [cysu = cysteinesulphinato(2−)-*SN*]. The chiroptical properties of potassium tris(L-cysu)cobaltate(III) were studied by Gillard and Maskill [14] who found stereospecific formation of only one isomer. Further, during the formation of the yellow product of peroxidation, the optical configuration was maintained. It had originally been found by Schubert [13] that, with the complex $[Co(en)_3]Br_3$, potassium (+)tris(L-cysu)cobaltate(III) formed an insoluble yellow compound formulated as $[Co(en)_3][Co(L\text{-}cysu)_3],7H_2O$; Gillard and Maskill repeated this experiment and found that the insoluble product contained the resolved ion $[Co(en)_3]^{3+}$. This paper reports the preparation and use of the complex $K_3(+)[Co(L\text{-}cysu)_3]$, with which we have successfully resolved a variety of 3+ species including the previously unresolved ions $[Rh(phen)_3]^{3+}$, $[Rh(bipy)_3]^{3+}$, and $[Rh(phen)_2(NH_3)_2]^{3+}$.

EXPERIMENTAL

Extinction coefficients and electronic spectra were measured with Unicam SP 500 (series 2) and 800 spectrophotometers, o.r.d. spectra with a Bendix NPL Polarmatic 62 spectropolarimeter, and c.d. spectra with a Roussel–Jouan model B Dichrographe. C, H, and N analyses were carried out by Mr. G. H. J. Powell, using a Hewlett–Packard model 185 C,H,N analyser, and percentage of water was estimated by means of a Stanton thermogravimetric balance with a d.t.a. attachment. Cobalt was determined following destruction of the cobalt(III) complex using conc. H_2SO_4–conc. HNO_3, spectrophotometrically as the thiocyanate, total chloride by oxygen-flask combustion, and ionic chloride by titration with mercury(II) nitrate.

Spectra.—All o.r.d. and c.d. spectra of the resolved species were determined at ambient temperature for aqueous solutions of the chloride salts. Extinction coefficients were determined for aqueous solutions of the perchlorate salts, with the exception of the ion $[Co(en)_2(phen)]^{3+}$ which was the bromide salt and that of $[Co(en)_2(bipy)]^{3+}$ which was the bromide diperchlorate salt.

Preparations.—*Potassium* (+)*tris*(L-*cysu*)*cobaltate*(III) *hexahydrate* [*cysu* = *cysteinesulphinato*(2−)-SN]. The complex $[Co(NH_3)_6]Cl_3$ (5·34 g, 0·02 mol) in water (140 cm³) was deoxygenated (N_2 bubbler) and then L-cysteine (12·12 g, 0·10 mol) and KOH (16·84 g, 0·30 mol) were added. The mixture was heated to 70 °C and, when no further evolution of ammonia could be detected (*ca.* 3 h), ethanol (140 cm³) was added, causing immediate precipitation of green † potassium tris(L-cysteinato-*SN*)cobaltate(III). The mixture was cooled (ice), rapidly filtered, and the solid washed with ethanol (2 × 70 cm³). The precipitate was then added slowly to H_2O_2 (100 vol., 100 cm³), the temperature being maintained below 10 °C; a rapid reaction ensued, giving a bright yellow solution. On addition of ethanol (200 cm³), immediate precipitation of the complex $K_3(+)[Co(L\text{-}cysu)_3]$ occurred; it was washed with ethanol (2 × 50 cm³) and then recrystallised in the dark from water–ethanol (2 : 1), giving hair-like crystals. Further product could be obtained on addition of more ethanol. The product was dried in the dark *in vacuo* over P_2O_5 for 24 h (Found: C, 14·7; H, 2·7; N, 5·8; H_2O, 14·4. Calc. for $C_9H_{27}CoK_3$-

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* Few subsequent applications of this method to organic molecules have been reported, although more recently Dwyer *et al.*[4] applied it to the resolution of certain amino-acids.

† It is interesting that in recent accounts of 'linkage isomerism,' the well known isomers (red and green) of cobalt(III)–cysteine complexes are never mentioned.

[3] A. Werner and M. Basyrin, *Ber.*, 1913, **46**, 3229.

[4] (*a*) F. P. Dwyer and B. Halpern, *Nature*, 1962, **196**, 270; (*b*) F. P. Dwyer, B. Halpern, and K. R. Turnbull, *Austral. J. Chem.*, 1963, **16**, 510.

[5] F. Basolo, *Co-ordination Chem. Rev.*, 1968, **3**, 213.

[6] F. P. Dwyer and F. L. Garvan, *Inorg. Synth.*, 1960, **6**, 192.

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

[8] J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, 1969, **8**, 1201.

[9] R. D. Gillard, P. R. Mitchell, and M. G. Price, *J.C.S. Dalton*, 1972, 1211.

[10] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 959.

[11] J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, 1969, **8**, 771.

[12] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 170.

[13] M. P. Schubert, *J. Amer. Chem. Soc.*, 1933, **55**, 3336.

[14] R. D. Gillard and R. Maskill, *Chem. Comm.*, 1968, 160.

$N_3O_{18}S_3$: C, 14·7; H, 3·7; N, 5·7; H_2O, 14·7%). The stereoisomeric structure of the complex was not determined, although the simplicity of its p.m.r. spectrum in D_2O indicated that it is probably an *abc*- rather than a ' non equivalent ' *abd*-isomer. Absorption and chiroptical spectra (Figure 1) were run on freshly prepared solutions; details of the maxima are given in Table 1.

TABLE 1

Absorption, o.r.d., and c.d. data and results

	Absorption		O.r.d.		C.d.	
Complex	λ/nm	$\varepsilon_{max.}$/l mol^{-1} cm^{-1}	λ/nm	$10^{-4}[\phi]$/°	λ/nm	Δε/l mol^{-1} cm^{-1}
$K_3(+)[Co(L\text{-}cysu)_3]$	406	824	476	−0·0885	438	−3·83
	308	29,000	417	+2·11	392	+3·75
			350	+2·52	316	+16·2
			294	−7·30	274	−11·9
$D(+)_{500}[Co(en)_2(phen)]^{3+}$	463	104	505	+0·5	483	+4·08
	349	735	435(sh)	−1·15	316	−3·24
	334(sh)	1210	303	−2·57	272	−17·1
	317(sh)	3010	278	−4·67		
	305(sh)	6110				
	273	30,250				
$D(+)_{546·1}[Co(en)_2(bipy)]^{3+}$	463	106	505	+0·53	483	+3·32
	319(sh)	10,100	440	−1·08	315	−7·96
	309	12,400	323	−2·96		
	299(sh)	10,300				
$D(+)_{546·1}[Co(phen)_3]^{3+}$	470(sh) [a]	86·9	502	+1·47	492	+1·29
	348	3680	352	+9·20	378	−3·93
	334(sh)	4650	335(sh)	+10·6	347	+4·50
	303	19,200	308	+22·8	330(sh)	+8·45
	280	70,500	288	+24·0	318(sh)	+12·6
	274	69,500	276	−123	302(sh)	+39·6
					283	+223
					269	−140
$D(+)_{546·1}[Co(bipy)_3]^{3+}$	450	79·5	516	+0·376	504	+0·346
	318	31,000	475	−0·083	450	−3·33
	306	34,100	440(sh)	+1·20	321	+104
			323	+22·6	299	−59·2
			316(sh)	−27·6		
			306	−37·0		
$D(+)_{400}[Rh(phen)_3]^{3+}$ [b]	350	3610	352	+7·80	346	+5·78
	334	4010	333	+9·30	331	+8·75
	317(sh)	8000	317(sh)	+13·6	302	+48·5
	303	20,700	308	+22·5	281	+302
	297(sh)	84,300	292(sh)	+23·3	266	−178
	273	84,300	284	+31·7		
			274	−157		
$D(+)_{350}[Rh(bipy)_3]^{3+}$ [b]	318	36,000	322	+36·7	321	+145
	305	35,000	315	−31·7	309(sh)	+52·1
	295(sh)	22,800	303	−37·8	300(sh)	−37·7
			295(sh)	−17·7	291	−57·9
$D(+)_{400}[Rh(phen)_2(NH_3)_2]^{3+}$ [b]	349	1890	351	+3·33	350	+1·88
	333	2260	333	+4·06	331	+2·79
	315(sh)	5300	307	+11·0	305(sh)	+20·0
	301	14,400	284	+12·5	280	+120
	280(sh)	43,400	273	−60·2	265	−60·0
	272	56,500				

[a] Ref. 22. [b] Molar absorption coefficients of these complexes were obtained from ref. 18.

Schubert [13] reported isolating the complex $K_3(+)$-$[Co(L\text{-}cysu)_3]$ as its trihydrate. Thermogravimetric and C and N analysis * have shown our complex to be the hexahydrate. Three molecules of water were removed relatively easily (*ca.* 80 °C) and remaining molecules removed gradually up to *ca.* 200 °C, at which temperature the compound decomposed. The complex was photo-labile, the surface of the solid becoming reddish in sunlight and an aqueous solution, if left in bright sunlight, showed a marked change in chiroptical properties. The absorption maximum at 406 nm disappeared and a new, but less intense, peak was observed at *ca.* 490 nm accompanied by a decrease in the intensity of the higher-energy peak at 308 nm. The c.d. spectrum also showed a marked change, the negative peak at 438 nm disappearing with the formation of a new negative peak at *ca.* 496 nm. A solution stored in the dark for the same period showed no changes in spectra, even when heated on a steam bath for several hours. The nature of the product of photolysis has not yet been investigated. It does seem that the complex is rather prone to form cobalt(II); an apparent thermochromism (yellow $\overset{\text{heat}}{\rightleftharpoons}$ green) of a solution in the presence of lithium chloride arises from the formation of a little cobalt(II), since hot solutions showed spectra typical of tetrahedral chlorocobaltate(II) species.

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* Anomalous H values are commonly obtained with our C, H, N, analyser for compounds with loosely held water of crystallisation.

Bis(ethylenediamine)(1,10-*phenanthroline*)*cobalt*(III) *bromide*. The complex [Co(en)$_2$(phen)]Br$_3$ was prepared according to the method of Gillard *et al.*[15] (Found: C, 32·1; H, 4·1; N, 14·0. Calc. for $C_{16}H_{24}Br_3CoN_6$: C, 32·0; H, 4·0; N, 14·0%).

(2,2′-*Bipyridyl*)*bis*(*ethylenediamine*)*cobalt*(III) *bromide diperchlorate*. The complex [Co(en)$_2$(bipy)]Br$_3$ was prepared using the above method for [Co(en)$_2$(phen)]Br$_3$, employing the ligand 2,2′-bipyridyl (0·78 g, 5 mmol) instead of 1,10-phenanthroline. To a hot solution of the resulting bromide salt was added a concentrated solution of NaClO$_4$. Orange-yellow crystals of the complex [Co(en)$_2$(bipy)]Br(ClO$_4$)$_2$ formed and were recrystallised twice from hot water (Found: C, 27·5; H, 4·1; N, 13·6. Calc. for $C_{14}H_{24}BrCl_2CoN_6O_8$: C, 27·4; H, 3·95; N, 13·7%).

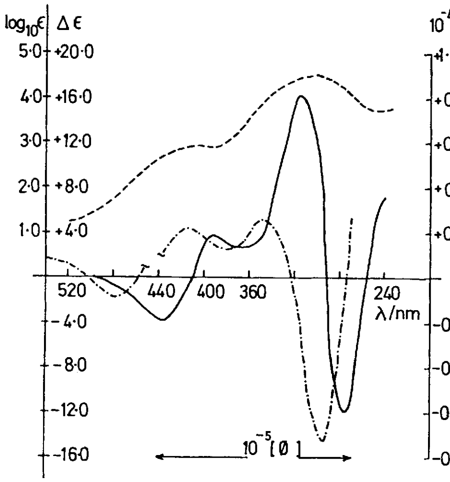

FIGURE 1 Absorption (– – – –), o.r.d. (— · — · —), and c.d. (——) spectra of the complex K$_3$(+)[Co(L-cysu)$_3$]

The unusual nature of the mixed anions in this novel 'double salt' prompted us to carry out the following further experiments. {It is noteworthy that the double salt [Co(en)$_2$(phen)]Cl(SO$_4$),2H$_2$O was prepared by Jaeger[16] and Hidaka *et al.*[17]}. A solution of the bromide diperchlorate salt was converted to the trichloride salt by anion exchange; on addition of a concentrated solution of NaClO$_4$, it afforded orange-yellow crystals of the complex [Co(en)$_2$(bipy)]Cl(ClO$_4$)$_2$,$\frac{1}{2}$H$_2$O which were recrystallised twice from hot water (Found: C, 28·8; H, 4·3; total Cl, 18·4; Cl$^-$, 6·1; Co, 10·1; N, 14·5. Calc. for $C_{14}H_{25}Cl_3CoN_6O_{8.5}$: C, 29·0; H, 4·4; total Cl, 18·4; Cl$^-$, 6·1; Co, 10·2; N, 14·5%). Its i.r. spectrum (Nujol mulls) showed bands at: 3100—3240mbr; 1610w; 1595m; 1570w; 1505w; 1316w; 1295vw; 1275w; 1245w; 1170m; 1135sh; 1055—1110vs,br; 1025sh; 965vw; 930vw; 895vw; 815w; 805w; 765vs; 645vw; 620vs; 590w; and 515w cm^{-1}.

Tris(1,10-*phenanthroline*)*cobalt*(III) *perchlorate trihydrate*. To CoCl$_2$,6H$_2$O (2·0 g, 8·4 mmol) in water (40 cm^3) was added a solution of 1,10-phenanthroline hydrate (5·0 g, 25·5 mmol) in methanol (5 cm^3). The mixture was set to reflux for 30 min with Br$_2$ water (20 cm^3). HClO$_4$ (70%, 20 cm^3) was then added to the hot solution whereupon yellow crystals of the complex [Co(phen)$_3$](ClO$_4$)$_3$,3H$_2$O immediately formed. The suspension was cooled (ice) and the product collected and recrystallised twice from hot water (Found: C, 45·8; H, 3·2; N, 8·9. Calc. for $C_{36}H_{30}Cl_3CoN_6O_{15}$: C, 45·4; H, 3·2; N, 8·8%).

Tris(2,2′-*bipyridyl*)*cobalt*(III) *perchlorate trihydrate*. The complex [Co(bipy)$_3$](ClO$_4$)$_3$,3H$_2$O was prepared using the above method, employing the ligand 2,2′-bipyridyl (4·0 g, 25·5 mmol) instead of that of 1,10-phenanthroline (Found: C, 40·9; H, 3·0; N, 9·50. Calc. for $C_{30}H_{30}Cl_3CoN_6O_{15}$: C, 40·9; H, 3·4; N, 9·55% *).

Rhodium(III) *complexes*. The complexes [Rh(phen)$_3$](ClO$_4$)$_3$,3H$_2$O, [Rh(bipy)$_3$](ClO$_4$)$_3$,2H$_2$O, and [Rh(phen)$_2$(NH$_3$)$_2$](ClO$_4$)$_3$,3H$_2$O were prepared as in ref. 18.

General Procedure for Resolutions.—The complex to be resolved was converted to its chloride salt by anion exchange (Deacidite FF-19 resin, Cl$^-$ form). To a hot solution of the racemic chloride salt was added sufficient of a concentrated solution of the complex K$_3$(+)[Co(L-cysu)$_3$] to give the ratio 2 mole racemate : 1 mole K$_3$(+)[Co(L-cysu)$_3$]. The resulting solution was cooled (ice) and a yellow precipitate of the less soluble diastereoisomer rapidly formed. The precipitate was collected and recrystallised four times from hot water. The final fraction was redissolved in hot water and reconverted to the chloride salt; all chiroptical measurements were made on this solution.

Analyses for the diastereoisomers of the ion [Co(en)$_3$]$^{3+}$ (Found: C, 20·9; H, 4·8; N, 14·3. Calc. for $C_{15}H_{53}Co_2N_9O_{19}S_3$: C, 20·5; H, 6·1; N, 14·4% *) and that of [Co(en)$_2$(phen)]$^{3+}$ (Found: C, 30·4: H, 4·3; N, 12·8. Calc. for $C_{25}H_{53}Co_2N_9O_{19}S_3$: C, 30·1; H, 5·4; N, 12·6% *) indicated 1 : 1 salts with seven water molecules of crystallisation.

RESULTS

Bis(ethylenediamine)(1,10-*phenanthroline*)*cobalt*(III).—The complex [Co(en)$_2$(phen)]$^{3+}$ was first resolved by Jaeger[16] using silver (+)bromocamphorsulphonate, Ag(+)bcs, and then repeated by Hidaka and Douglas[17] who reported for the complex (−)[Co(en)$_2$(phen)]I$_3$ a specific rotation $[\alpha]_{543}$ −240° compared with Jaeger's value of −235°. Hidaki and Douglas also measured the absorption and c.d. spectra of this complex ($\varepsilon_{max.}$ 118 at 465 and Δε −2·78 l mol^{-1} cm^{-1} at 480 nm †). Gillard *et al.*[15] improved the degree of resolution slightly using NH$_4$(+)bcs and reported $\varepsilon_{max.}$ *ca.* 100 at 465 and Δε *ca.* −3·2 l mol^{-1} cm^{-1} at 480 nm.

Employing NH$_4$(+)bcs we have resolved the ion [Co(en)$_2$(phen)]$^{3+}$, recrystallising the less soluble diastereoisomer {which contains (−)[Co(en)$_2$(phen)]$^{3+}$} until optical constancy was achieved. The chloride salt was prepared and its o.r.d. and c.d. spectra measured ($\varepsilon_{max.}$ 104 at 463 and Δε −4·08 l mol^{-1} cm^{-1} at 483 nm). This ion was also resolved using K$_3$(+)[Co(L-cysu)$_3$] as the resolving agent; the spectra obtained were enantiomeric, *i.e.* the complex

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* Footnote as on page 935.

† The value given in Table 1 of ref. 17 is −7·8 l mol^{-1} cm^{-1} but Douglas[19] confirms that this is a misprint and should read −2·78 l mol^{-1} cm^{-1}. However the value −7·8 has been misquoted as −0·78 in ref. 20. This last value also appears in ref. 21. The correct value for optically pure [Co(en)$_2$(phen)]Cl$_3$ as determined here is −4·08 l mol^{-1} cm^{-1}.

[15] R. D. Gillard, R. E. E. Hill, and R. Maskill, *J. Chem. Soc.* (*A*), 1970, 1447.

[16] F. M. Jaeger, *Proc. Roy. Acad. Sci. Amsterdam*, 1926, **29**, 559.

[17] J. Hidaka and B. E. Douglas, *Inorg. Chem.*, 1964, **3**, 1180.

[18] P. M. Gidney, R. D. Gillard, and B. T. Heaton, *J.C.S. Dalton*, 1972, 2621.

[19] B. E. Douglas, personal communication.

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

[21] C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley-Interscience, New York, 1971, 218.

(+)[Co(en)$_2$(phen)](+)[Co(L-cysu)$_3$] crystallised but the spectral details were identical (Table 1) to those on resolution with NH$_4$(+)bcs.

Although the Δε values are considerably higher than any previously reported, the extinction coefficient at 463 nm is significantly lower than that obtained by Hidaka and Douglas. We believe that this inconsistency can be attributed (at least in part) to the difference in the counter-ions used. Like Jaeger, Hidaka and Douglas used iodide as counter-ion, the charge-transfer effect of which could explain the high extinction coefficient. The chiroptical profiles (Figure 2) for the enantiomer of [Co(en)$_2$(phen)]$^{3+}$ giving the less soluble diastereoisomer with (+)[Co(L-cysu)$_3$]$^{3-}$ are consistent with its having the D-configuration.

(2,2′-Bipyridyl)bis(ethylenediamine)cobalt(III).—The complex [Co(en)$_2$(bipy)]$^{3+}$ was partly resolved by McCaffery *et al.*[20] using the ion (−)[Co(ox)$_3$]$^{3-}$ as the resolving agent ($\varepsilon_{max.}$ 114 at 456 and Δε − 0·95 l mol^{-1} cm^{-1} at 480 nm for the iodide salt of the bipy complex). We have resolved the ion [Co(en)$_2$(bipy)]$^{3+}$ using the complex K$_3$(+)[Co(L-cysu)$_3$], recrystallising the less soluble diastereoisomer until optical constancy was achieved. The chloride salt was prepared ($\varepsilon_{max.}$ 106 at 463 and Δε +3·32 l mol^{-1} cm^{-1} at 483 nm, Table 1). No resolution was achieved with NH$_4$(+)bcs. The optical purity is considerably higher than that obtained by earlier workers; this is not surprising as the resolving agent previously used, (−)[Co(ox)$_3$]$^{3-}$, is heat labile and racemises completely in solution within 24 h.[22]

The position, and magnitude of the molar extinction coefficient, of the lowest-energy *d–d* band of the complex [Co(en)$_2$(bipy)]$^{3+}$ are reported by McCaffery *et al.*[20] as 456 nm and 114 l mol^{-1} cm^{-1} respectively. We find the band maximum at 463 nm which agrees with the corresponding value for [Co(en)$_2$(phen)]$^{3+}$ obtained previously.[15,17] Further, the magnitude of the molar extinction coefficient is greater than that of our value, but again this can be attributed (certainly in part) to the use of iodide as the counter-ion. The spectroscopic profiles (Figure 3) for the enantiomer of the ion [Co(en)$_2$(bipy)]$^{3+}$ giving the less soluble diastereoisomer with the complex K$_3$(+)[Co(L-cysu)$_3$] are consistent with it having the D-configuration.

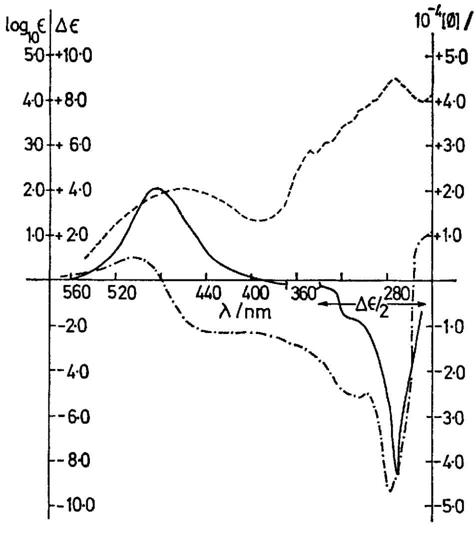

FIGURE 2 Absorption (– – – –), o.r.d. (— · — · —), and c.d. (——) spectra of the complex D(+)$_{500}$[Co(en)$_2$(phen)]$^{3+}$

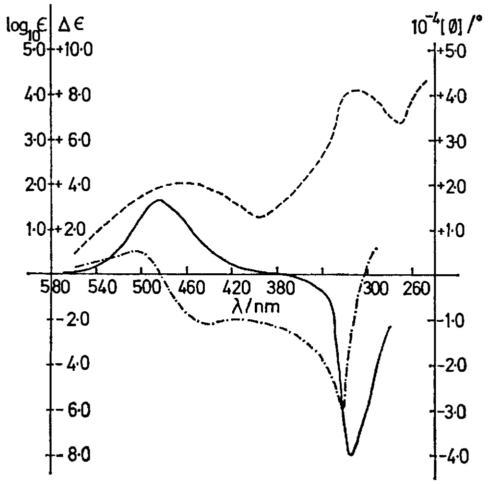

FIGURE 3 Absorption (– – – –), o.r.d. (— · — · —), and c.d. (——) spectra of the complex D(+)$_{546\cdot1}$[Co(en)$_2$(bipy)]$^{3+}$

Tris(1,10-*phenanthroline*)*cobalt*(III) *and Tris*(2,2′-*bipyridyl*)*cobalt*(III).—Partial resolution of the ion [Co(phen)$_3$]$^{3+}$ was achieved by Lee *et al.*[23] using silver (+)tartrato(4−)-antimonate(III), following an unsuccessful attempt by other workers.[24] The method most commonly used to obtain optically active tris-(1,10-phenanthroline) and -(2,2′-bipyridyl) complexes of metals in oxidation state III is by oxidation of the corresponding optically active metal(II) complex.[10] Using this approach, Ferguson *et al.*[11] * prepared the complexes D(+)[Co(phen)$_3$](ClO$_4$)$_3$,3H$_2$O and L(−)[Co(bipy)$_3$](ClO$_4$)$_3$,2H$_2$O and reported Δε values of +222 at 282 and −111·1 l mol^{-1} cm^{-1} at 318 nm respectively.

We have resolved both the complexes [Co(phen)$_3$]$^{3+}$ and [Co(bipy)$_3$]$^{3+}$ with K$_3$(+)[Co(L-cysu)$_3$] and values obtained for the cations of the less soluble diastereoisomers as chloride salts were Δε +223 at 283 and Δε +104 l mol^{-1} cm^{-1} at 321 nm respectively (Table 1). Spectroscopic profiles show a close correlation with those reported by Ferguson *et al.*[11] and with both species the D-configuration of the cation gave the less soluble diastereoisomer, though, as we pointed out some years ago,[26] no great significance attaches to this fact, in the absence of information on the relevant crystal lattices.

Tris(1,10-*phenanthroline*)*rhodium*(III) *and Tris*(2,2′-*bipyridyl*)*rhodium*(III).—Previous attempts at resolving tris-(1,10-phenanthroline) and -(2,2′-bipyridyl) complexes of rhodium(III) with tartrate, lactate, citrate (*sic*), nitrocamphorate, camphorate, antimony(III), (+)-tartrate, camphorsulphonate, and bcs [27] or by a chromatographic technique [18]

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* Ref. 11 attributes the spectra obtained for the complex (+)[Co(phen)$_3$]$^{3+}$ to the L-configuration and (−)[Co(bipy)$_3$]$^{3+}$ to the D-configuration; it has since been shown [25] that both assignments are incorrect, the spectra are in fact those of D- and L-complexes respectively.

[22] G. B. Kauffman, L. T. Takahashi, and N. Sugisaka, *Inorg. Synth.*, 1966, **8**, 207.

[23] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Hunt, *Inorg. Chem.*, 1966, **5**, 1397.

[24] P. Ellis, R. G. Wilkins, and M. J. G. Williams, *J. Chem. Soc.*, 1957, 4456.

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

[26] K. Garbett and R. D. Gillard, *J. Chem. Soc.* (*A*), 1966, 802.

[27] E. D. McKenzie and R. A. Plowman, *J. Inorg. Nuclear Chem.*, 1970, **32**, 199.

were unsuccessful. Both the complexes $[Rh(phen)_3]^{3+}$ and $[Rh(bipy)_3]^{3+}$ were successfully resolved using $K_3(+)$-$[Co(L\text{-}cysu)_3]$. The similarity of the chiroptical profiles of the enantiomer of the complex $[Rh(phen)_3]^{3+}$ giving the less soluble diastereoisomer (Figure 4) to those of D-$[Co(phen)_3]^{3+}$ (Figure 5) are consistent with the rhodium species having the D-configuration.

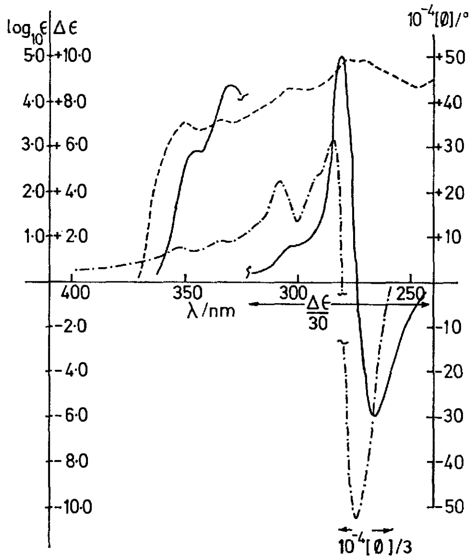

FIGURE 4 Absorption (– – – –), o.r.d. (— • — • —), and c.d. (——) spectra of the complex $D(+)_{400}[Rh(phen)_3]^{3+}$

The analogous 2,2′-bipyridyl complex also appears to have the D-configuration but its spectral profiles in the u.v. region (Figure 6) show departures from those of D-$[Co(bipy)_3]^{3+}$ (Figure 7). Whereas both these bipy complexes have a common positive o.r.d. peak at *ca.* 322 nm, two distinct negative peaks are observed at 315 and 303 nm for the rhodium(III) complex as compared with one peak at 306 nm and a small shoulder at 316 nm for the cobalt(III) complex. The c.d. curve for the former complex has a pronounced positive shoulder at 310 nm and the negative peak at 291 nm is diminished in proportion to the high positive peak at 321 nm, compared with the analogous peaks for D-$[Co(bipy)_3]^{3+}$ (Table 1). We believe the anomalous o.r.d. and c.d. spectra for the complex D-$[Rh(bipy)_3]^{3+}$ result from the ligand π–π^* absorption and the absorption due to the lowest-energy *d–d* band of rhodium(III) in the $[RhN_6]$ chromophore which occur in the same region.

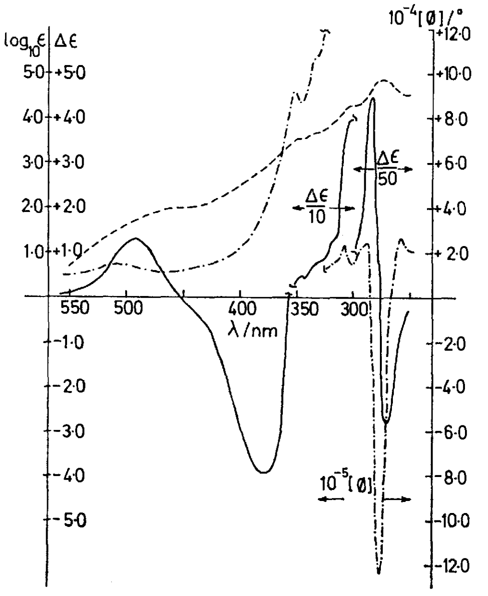

FIGURE 5 Absorption (– – – –), o.r.d. (— • — • —), and c.d. (——) spectra of the complex $D(+)_{546 \cdot 1}[Co(phen)_3]^{3+}$

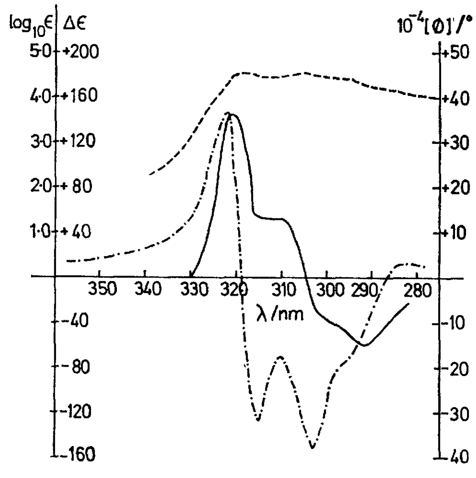

FIGURE 6 Absorption (– – – –), o.r.d. (— • — • —), and c.d. (——) spectra of the complex $D(+)_{350}[Rh(bipy)_3]^{3+}$

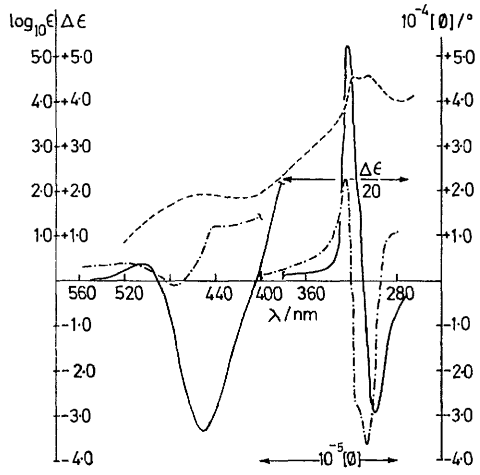

FIGURE 7 Absorption (– – – –), o.r.d. (— • — • —), and c.d. (——) spectra of the complex $D(+)_{546 \cdot 1}[Co(bipy)_3]^{3+}$

cis-*Diamminebis*(1,10-*phenanthroline*)*rhodium*(III).— Synthesis of the complex $[Rh(phen)_2(NH_3)_2](ClO_4)_3,3H_2O$ has recently been reported [18] but no attempt was made to resolve it. Employing the complex $K_3(+)[Co(L\text{-}cysu)_3]$, the rhodium complex was readily resolved and the enantiomer having the D-configuration formed the less soluble diastereoisomer. Details of the maxima are given in Table 1 and spectral profiles in Figure 8.

Tris(*ethylenediamine*)*cobalt*(III).—When the first studies were made of the diastereoisomers $[Co(en)_3][Co(L\text{-}cysu)_3]$ (ref. 28) we reported [14] that $L(-)[Co(en)_3]^{3+}$ formed the

[28] R. Maskill, Ph.D. Thesis, University of Kent at Canterbury, 1970.

less soluble salt. This is *not* correct. We have now repeatedly and consistently established that when 1 *mole* of the complex $K_3(+)[Co(L\text{-}cysu)_3]$ is added to 2 moles of $DL[Co(en)_3]^{3+}$, the precipitate contains mainly the complex $D(+)[Co(en)_3]^{3+}$.

The diastereoisomer was originally prepared [29] by adding an excess of the complex $DL[Co(en)_3]Cl_3$ dissolved in the minimum of water to the complex $K_3(+)[Co(L\text{-}cysu)_3]$ (0·5 g) dissolved in the minimum of water. A yellow precipitate was immediately deposited. This was recrystallised from hot water whereupon fine yellow crystals resulted. We have re-examined this original sample and it undoubtedly contains predominantly $L(-)[Co(en)_3]^{3+}$. Both diastereoisomers have low solubility,[13] although the $D(+)$-diastereoisomer is far less soluble than the $L(-)$, so that the error probably arose as follows. Assuming that sufficient of the complex $K_3(+)[Co(L\text{-}cysu)_3]$ was in fact employed to give essentially complete precipitation (*i.e.* the mole ratios were approximately 1 : 1), then roughly equal amounts of the $D(+)[Co(en)_3]^{3+}$ and $L\text{-}(-)[Co(en)_3]^{3+}$ diastereoisomers would have been present in the solid. During recrystallisation, the supernatant liquid would contain mostly the $L(-)$-diastereoisomer, and if the solid obtained from the filtrate was examined, then a predominance of this diastereoisomer would have been found which would have been wrongly thought to arise from the less soluble diastereoisomer.

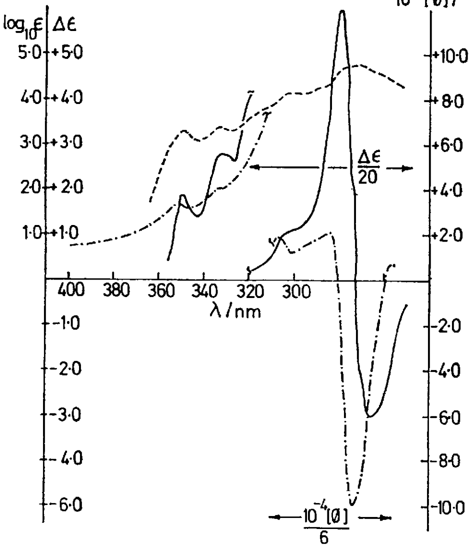

FIGURE 8 Absorption (– – – –), o.r.d. (— · — · —), and c.d. (——) spectra of the complex $D(+)_{400}[Rh(phen)_2(NH_3)_2]^{3+}$

Miscellaneous Resolutions.—To demonstrate the versatility of the complex $K_3(+)[Co(L\text{-}cysu)_3]$, it was successfully used to resolve, on a qualitative basis, a variety of other 3+ species and one 6+ species. It was found (Table 2) that the D-forms of the complexes $[Co(en)_3]^{3+}$, $[Co(\pm pn)_3]^{3+}$ (pn = propylenediamine), $[Cr(en)_3]^{3+}$, and $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ gave the less soluble diastereoisomer whereas it was the L-forms of the complexes $[Co(tn)_3]^{3+}$ (tn = trimethylenediamine), $[Cr(\pm pn)_3]^{3+}$, and $[Rh(\pm pn)_3]^{3+}$ which gave the less soluble diastereoisomer. In the past a variety of agents have been used to resolve these species including the ions (+)- and (−)-tartrate,[30-32] nitrocamphorate,[33,34] and (+)tartrato(4−)antimonate(III).[35] It should be noted that the complexes $[Co(\pm pn)_3]^{3+}$, $[Cr(\pm pn)_3]^{3+}$, $[Rh(\pm pn)_3]^{3+}$, and $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ are all mixtures of isomers and the resulting c.d. spectra obtained were consequences of all the isomers present in each sample.

TABLE 2

Sign of c.d. and absolute configuration of the isomer forming the less soluble diastereoisomer with the complex $(+)[Co(L\text{-}cysu)_3]^{3-}$

Complex	λ/nm	Sign of c.d.	Absolute configuration
$[Co(en)_3]^{3+}$	490	+	D [a]
$[Co(\pm pn)_3]^{3+}$	472	+	D [b]
$[Co(tn)_3]^{3+}$	470	+	L [c]
$[Cr(en)_3]^{3+}$	456	+	D
$[Cr(\pm pn)_3]^{3+}$	466	−	L
$[Rh(\pm pn)_3]^{3+}$	316	−	L
$[Co\{(OH)_2Co(en)_2\}_3]^{6+}$	606	+	D [d]

[a] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 795. [b] H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, 1966, **39**, 92. [c] Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Japan*, 1968, **41**, 530; J. R. Gollogly and C. J. Hawkins, *Chem. Comm.*, 1968, 689. [d] S. F. Mason and J. W. Wood, *Chem. Comm.*, 1967, 209.

In the series $[M(\pm pn)_3]^{3+}$ the less soluble diastereoisomer contained a D-form of the complex $[Co(\pm pn)_3]^{3+}$ but an L-form of those of $[Cr(\pm pn)_3]^{3+}$ and $[Rh(\pm pn)_3]^{3+}$. This might seem at variance with the Werner–Jaeger [36,37] theory which proposes that if two complex ions give less soluble isomorphous diastereoisomers with a given resolving counter-ion, then they have related configurations. However, the ion $[M(\pm pn)_3]^{3+}$ is not a simple system; it is well known that in complexes of transition metals with optically active diamine ligands there are marked stereoselective effects. From an equilibrated sample of the complex $[Co(\pm pn)_3]^{3+}$, Dwyer *et al.*[31] separated eight diastereoisomers (four pairs of enantiomers) and determined their equilibrium concentrations (Table 3). They were not able to tell whether the enantiomers were *cis*(*abc*) or *trans*(*abd*), or a mixture of the two. More recently both MacDermott [38] and Crossing and Snow [39] have shown that physical properties of the *cis*- and *trans*-isomers of $L[Co(-pn)_3]Cl_3$ are

TABLE 3

Equilibrium racemic pair concentrations for the complex $DL[Co(\pm pn)_3]^{3+}$, as determined by Dwyer *et al.*[31]

Racemic pairs		Isomer concentration/%
$D[Co(+++)]$	$L[Co(---)]$	40·5
$D[Co(++-)]$	$L[Co(--+)]$	40·3
$D[Co(+--)]$	$L[Co(-++)]$	16·5
$D[Co(---)]$	$L[Co(+++)]$	2·7

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[29] R. Maskill, personal communication.

[30] D. H. Busch, *J. Amer. Chem. Soc.*, 1955, **77**, 2747.

[31] F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Amer. Chem. Soc.*, 1964, **86**, 590.

[32] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 1965, 2883.

[33] A. Werner, *Ber.*, 1912, **45**, 865.

[34] F. Woldbye, *Optical Rotatory Dispersion of Transition Metal Complexes*, European Research Office, U.S. Army, Frankfurt, 1959.

[35] H. A. Goodwin, E. C. Gyarfas, and D. P. Mellor, *Austral. J. Chem.*, 1958, **11**, 426.

[36] A. Werner, *Bull. Soc. chim. France*, 1912, **11**, 1.

[37] F. M. Jaeger, *Bull. Soc. chim. France*, 1937, **4**, 1201.

[38] T. E. MacDermott, *Inorg. Chim. Acta*, 1968, **2**, 81.

[39] P. F. Crossing and M. R. Snow, *J.C.S. Dalton*, 1972, 295.

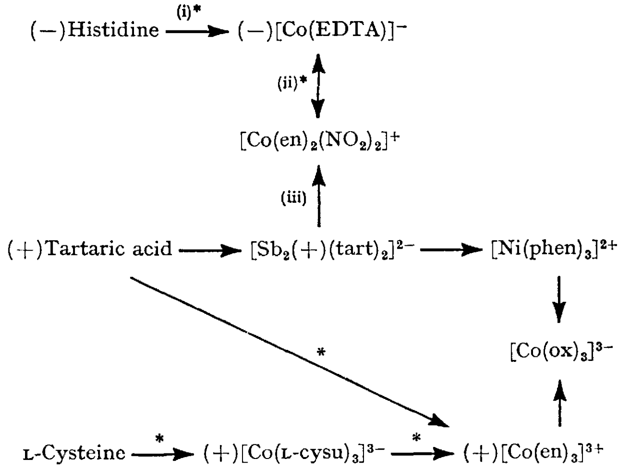
very similar and MacDermott [38] showed the ratio of *cis* to *trans* was 1 : 3, that expected statistically.

The samples of the complexes $[Co(\pm pn)_3]^{3+}$, $[Cr(\pm pn)_3]^{3+}$, and $[Rh(\pm pn)_3]^{3+}$ used were not deliberately equilibrated during preparation. Even assuming that the same ratio of geometrical isomers was obtained for each metal ion, it is unlikely that the racemic pair ratios for the complex $[Co(\pm pn)_3]^{3+}$ would be the same as those given in Table 3. Further, it is possible that such ratios for the complexes $[Cr(\pm pn)_3]^{3+}$ and $[Rh(\pm pn)_3]^{3+}$ differ from those of $[Co(\pm pn)_3]^{3+}$. If this is so, then it is not too surprising that the complex $(+)[Co(L\text{-}cysu)_3]^{3-}$ precipitates differing isomers for cobalt as compared with rhodium or chromium complexes, and the present results do not constitute a comment on the validity of the Werner–Jaeger rule.

DISCUSSION

Any resolution of optical isomers in the laboratory depends on the use of a natural product. The best resolutions *via* diastereoisomeric salts are those which involve cheap natural products and a clean, convenient separation of the resulting diastereoisomers. We use the term 'resolving relay' to denote an asymmetric agent which is conveniently available in bulk (*ca.* 50—100 g) from cheap natural products, either *via* a neat resolution or a convenient asymmetric synthesis.

Resolving relays may be used for further resolutions; some examples are given in the Scheme (* denotes a facile step). Steps (i) and (ii) provide a facile route to the resolved complex $[Co(en)_2(NO_2)_2]^+$ through the resolving relay $(-)[Co(EDTA)]^-$. This contrasts with an established,[6] but inconvenient and tedious, route of (iii) followed by (ii) as a means of resolving the complex $[Co(EDTA)]^-$. The complex $(-)[Co(ox)_3]^{3-}$ had been used as a 3— resolving agent with limited success. It is not really a resolving relay because it is arduous to resolve, racemising completely within 24 h, and it is thermally labile. A real need therefore existed for a 3— resolving agent with none of these drawbacks and the tris(L-cysu)cobaltate(III) complex described here may well prove generally useful.



SCHEME

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