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The Phenomenon of Conglomerate Crystallization.
X. New Classes of *Clavic* Coordination Compounds Crystallizing as Conglomerates and Enumeration of Further Factors Relevant to Conglomerate Behaviour

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Abstract

Octahedral Co(III) compounds of the sulfenyl and sulfinyl families, as well as their Se counterparts, have been found to readily undergo spontaneous resolution into crystalline conglomerates.

Examples of octahedral compounds of Co(III) containing $-S_2O_3$ and $-SO_3$ ligands have also been found to do so. In fact, despite their superficial chemical differences sulfenyls and sulfinyls share with these latter species simple stereochemical fragments which render both of them *clavic.*

An example of a *clavic* Ru-π-olefin, $[Ru(NH_3)_5(fumarate)]^{2+}$ cation, is discussed also.

From the variety of compounds discussed in this report, it is clear that the phenomenon described previously is not the province of a narrow class of compounds best classified as an interesting oddity.

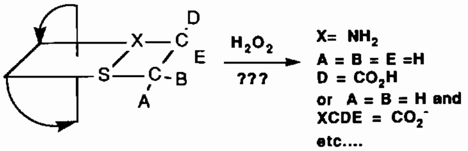
Introduction

In a series of papers [1–7] preceding this, we have demonstrated that racemic solutions of a class of compounds, labelled *clavic* [1], display a pronounced tendency towards forming crystalline conglomerates. For compounds of that class, the reproducibility and frequency of incidence of such a phenomenon was large enough to rule out statistical aberrations and a set of simple guidelines was found which predicted, reasonably accurately, when conglomerate crystallization should occur in the case of a variety of geometrical isomers of octahedral compounds of Co(III) [1–7].

It was suggested [1–7] that intramolecular interactions, such as hydrogen bonds, capable of locking ligands into relatively stable, dissymmetry-inducing conformations appear to be the source of their propensity for spontaneous resolutions into mechanical mixtures of chiral crystals, *i.e.* conglomerates.

Since the coordination compounds then dealt with were all nitro derivatives of Co(III) amines, it seemed desirable to explore the possibility that substances which, while belonging in the *clavic* category, would be chemically sufficiently different from the previous set to allow a test in generality of the conclusions previously reached. It is true the first report [1] demonstrated that suitable classes of organic compounds seemed also to fall in the same category and that even the limitation of being nitro derivatives did not apply since alcohols, amines, amides and thioamides were shown to frequently form conglomerates. However, for the purpose of this report, we would like to limit ourselves to octahedral compounds of the transition elements.

The current investigation was initiated when a brief, but important note by Jackson *et al.* [8] came to our attention. It concerns the hydrogen peroxide oxidation (Scheme 1) of species containing a bidentate linkage bearing a Co–S bond (see below). While true that this reaction had been studied earlier by others [9–12], the chiroptical properties of the products had not been clearly defined by the investigations prior to that of Jackson *et al.* [8] who demonstrated by optical and X-ray measurements that two sulfenates and one sulfinate could be isolated, the *clavic* behaviour of which is discussed below.



Scheme 1.

Table I has been constructed in order to summarize information which pertains to the problem we are addressing. The substances selected radically depart from those considered before [1–7] either because the ligands are chemically very different or because, in one case, the metal is Ru(II) and the clavic ligand is an olefin dicarboxylate (*i.e.* fumaric acid).

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TABLE I.

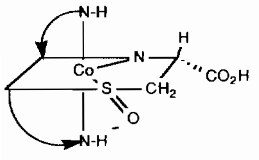
	Compound	Space group	Reference
(i)	$[Co(en)_2(cysteinsulfenato)](ClO_4)_2$	$P2_1$	8
(ii)	$[Co(en)_2(cysteinsulfenato)](ClO_4)$[a]	$P2_1$	8
(iii)	$[Co(en)_2(NH_2{-}CH_2{-}CH_2{-}S(O))](SCN)_2$	$P2_12_12_1$	13
(iv)	$[Co(en)_2(NH_2{-}CH_2{-}CH_2{-}S(O_2))](NO_3)(ClO_4)$	$P2_1$	10
(v)	$[Co(en)_2(NH_2{-}CH_2{-}CH_2{-}Se(O_2))](NO_3)_2$	$P2_1$	14
(vi)	$(en)_2Co[S(CHC(O)N(Et)COCH_2)CH_2CH_2S](ClO_4)_3$	$P2_1$	15
(vii)	$[cis\text{-}Co(en)_2(NO_2)(S\text{-}SO_3)]$	$P2_1$	16
(viii)	$NH_4[cis\text{-}Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$	$P2_12_12_1$	17[b]
(ix)	$[Ru(NH_3)_5(C_4H_4O_4)]S_2O_6\cdot 2H_2O$ $(C_4H_4O_4)$ = fumaric acid	$C222_1$	18

[a] Deprotonated $-CO_2H$. Molecules i and ii are present, simultaneously, in the same crystal. See original for details. [b] The structure of $NH_4[cis\text{-}Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$ was determined by three independent groups which agreed on the space group and cell constants; these are given in ref. 17.

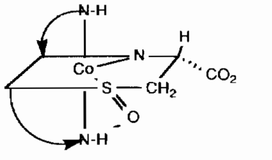
Discussion

(a) Sulfenyl and Sulfinyl Compounds and Their Se Analogues

Compounds **i** and **ii** differ by having an uncoordinated carboxylate which is protonated in the former and deprotonated in the latter, as schematically shown below



i. protonated



ii. deprotonated

Figure 2 of ref. 8 shows that, for both anions, the sulfenyl oxygen is so oriented as to form a hydrogen bond with the adjacent $-NH_2$ hydrogens. The reaction employed Λ-$[Co(en)_2(cystS)]^{2+}$, a diastereoisomer whose Λ configuration is retained throughout; however, the fact that these cations crystallize with a specific configuration at sulfur is, as we shall see below, an important observation in understanding the factors contributing to the phenomenon of conglomeration.

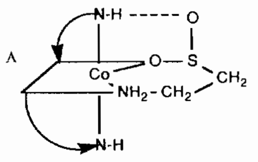
Shimura and his group have made fundamental contributions to the synthesis and the stereochemical behaviour of (N, S)-bonded, octahedral, Co(III) compounds [19–23]. Among them, the following:

(a) In solution [19], despite coordination to cobalt, the stereochemical stability at the S of anions $[Co(en)_2(NH_2{-}CH_2{-}CH_2{-}S\text{-alkyl})]^{3+}$ is low; this is demonstrated by the presence of a single ^1H NMR peak in the S–Me region. However, upon crystallization, the 'thioethers are coordinated stereoselectively. The *S*-alkyl group in the configuration Δ-(*R*) or Λ-(*S*) has appreciable non-bonded atomic interactions with the adjacent chelate ring in contrast to that in the Δ-(*S*) or Λ-(*R*). Thus, it is concluded that the configurations of the resolved complexes are Δ-(*S*) or Λ-(*R*).' Stereochemical preferences in this cases are, therefore, dictated by non-bonded repulsions.

(b) On the other hand, they concluded [21] that 'the (*R*) configuration of the sulfenato group is more stable than the (*S*) one in the *fac*(*S*)-Λ-[Co(sulfenato-$N,S)_n$(sulfinato-$N,S)_{3-n}$].' In the case of $n = 3$, the structure [20] shows all three sulfenyl oxygens directed towards the $-NH_2$ hydrogens on adjacent ethylenediamines. Thus, as in the above cases, this bonded interaction is present and it appears to be the origin of the configurational stereospecificity of an extended and complex family of compounds.

(c) In the case [22] of fac(*S*)-[Rh(sulfenato-$N,S)_n$-(sulfinato-$N,S)_{3-n}$] 'the (*R*) configuration of the sulfenato group is more stable than the (*S*) one in the Λ-isomer.'

(d) Synthesis and separation [23] of the diastereoisomers of chiral O-bonded sulfinates Λ-$[Co(NH_2{-}CH_2{-}CH_2{-}SO_2\text{-}N,O)(en)_2](ClO_4)_2$ revealed that the two species separated are Λ-(*R*) and the Λ-(*S*), where (*R*) and (*S*) refer to the chirality at the sulfur atom.



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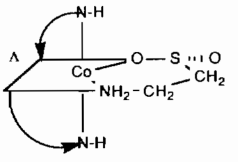
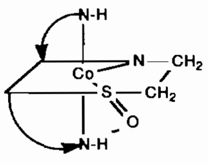


S

these interconvert into one another, while retaining at all times the Λ configuration at Co.

Throughout all the above studies, chiral ligands, chiral compounds of Co or external resolving agents were employed in the preparations of those samples used in the spectral or structural studies. Consequently, it was relevant to investigate related systems for which the reagents employed were racemic and no resolutions were carried out on the products. That is, if the products obtained were optically active crystals, clear proof of conglomerate behaviour was implied.

Compounds **iii** and **iv**, prepared from $[Co(en)_2(NH_2-CH_2-CH_2-S)]^{2+}$ were found by Deutsch and



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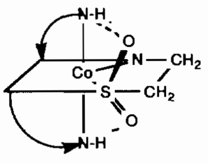

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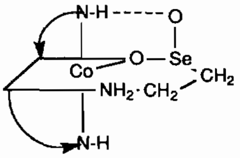
associates [13, 10] to crystallize, respectively, in the enantiomorphic space groups $P2_12_12_1$ and $P2_1$ and, since the thiol ligand is not a chiral species and the oxidations were carried out on racemic materials, it is clear that these are cases of conglomerate crystallization. Furthermore, Fig. 1 of both their original disclosures (refs. 13 and 10, respectively) reveal that the expected —SO....NH— intramolecular hydrogen bonding is, indeed, present in both cases. Thus, the S-bonded sulfinyl compound Jackson *et al.* [8] reported as the product of exhaustive oxidation of the (cysteinylS) derivative is expected to behave precisely as **iv** and to share the conformational and configurational specificity encountered by Shimura and associates [19–23].

Another clear and independent demonstration of the generality of the above principles is exemplified by **v** and **vi**, both of which form conglomerates, crystallizing in the enantiomorphic space group $P2_1$.



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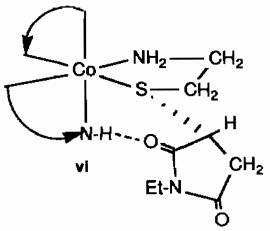


vi

Okamoto *et al.* [14] prepared the $-SeO_2$ compound **v** from racemic $[Co(en)_2(NH_2-CH_2-CH_2-Se)]^{2+}$ and clearly recognized the selenyl product crystallized as a conglomerate. Doedens *et al.* [15] prepared **vi** from racemic $[Co(en)_2(NH_2-CH_2-CH_2-S)]^{2+}$ and succinimide, and the product crystals contained a single diastereoisomer. Compound **v** has two chiral centers (Co and Se) while **vi** has three, *i.e.* the cobalt atom, the S and one of the carbon atoms of the imide ring.

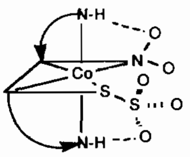
Given the experiences of Shimura *et al.* [19–23] with the relatively low stereochemical stability of sulfenyls and sulfinyls, the fact that Okamoto *et al.* [14] observed spontaneous resolution of **v** to a conglomerate of pure diastereoisomers is remarkable enough, even if the reaction had proceeded from a pre-resolved $[Co(en)_2(NH_2-CH_2-CH_2-Se)]^{2+}$ since a new, and relatively unstable, chiral center is created. The case of **vi** is even more impressive since each crystal contains a single stereoisomer despite the fact that the resulting solution should contain eight – four enantiomeric pairs.

It is also pertinent to the stereochemical behaviour of **vi** that the N-alkylated succinimide ring bears two carbonyl groups, one of which can be so oriented as to form a hydrogen bond with an $-NH_2$ of the adjacent ethylenediamine ligand, as diagrammatically shown in the sketch above. In fact, it does, as the reader can verify by referring to Fig. 1 of the original structural study. Thus, the alkylated succinimide ring can play the same *clavic* role as the $-NO_2$ groups present in those compounds in which the phenomenon was first noted [1–7].

Not inconsequentially, we find that the compound with Se–Me, instead of Se=O, does not spontaneously resolve into a crystalline conglomerate [24]. The authors prepared the compound by alkylation of optically active $[Co(en)_2(NH_2-CH_2-CH_2-Se)]^{2+}$ and found the resulting crystals to be optically active (space group $P2_1$), as in the case of the work of Shimura *et al.* [19–23] with the S analogues, and despite the stereochemical instability problems mentioned earlier. Okamoto *et al.* [24] determined the crystal structure and absolute configuration of a crystal of $[Co(en)_2(NH_2-CH_2-CH_2-Se-Me)]^{2+}$ which demonstrated that the conclusions of Shimura and associates [19–23] concerning the steric hindrance and stereochemical preferences of *S*-alkyl complexes are common with those of the related Se analogues.

(b) Other Related Co(III) Compounds

Compounds **vii** and **viii**, both of which contain ionic oxysulfur ligands, are stereochemically analogous to $[cis\text{-}Co(en)_2(NO_2)_2]Cl$; however, neither the thiosulfate nor the sulfite ligands had been noted to form conglomerates in our previous studies [1–7]. These substances are related, insofar as *clavic* behaviour, to those discussed above since all of them contain the fragments Co–E=O or $Co-E=O_2$, with E = S or Se; furthermore, **vii** and **viii** illustrate other



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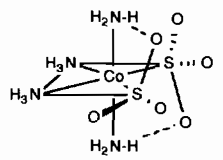


viii

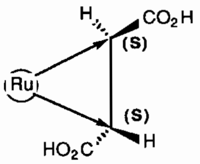
important concepts: (a) neutral species can readily form conglomerates (see **vii**) and (b) sulfite and thiosulfate, as expected, can act as *clavic* ligands.

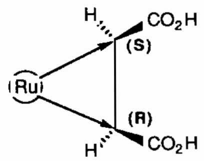
It would, therefore, not be unexpected to find that compounds containing different combinations of the same ligands, such as NH_4[*cis*-$Co(en)_2(SO_3)_2$], NH_4[*cis*-$Co(en)_2(SO_3)(S_2O_3)$], [*cis*-$Co(en)_2(NO_2)(SO_3)$], [*cis*-$Co(en)_2(NO_2)(S_2O_3)$] etc. are later reported to undergo conglomerate crystallization.

(c) Conglomerate Crystallization of Ru(II) Compounds

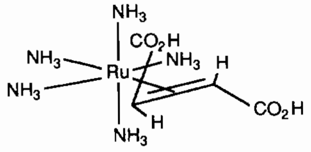
In 1979, Ludi and collaborators [18] examined the products of reacting $[Ru(NH_3)_5H_2O]^{2+}$ with a variety of olefins, among them fumaric acid.

If we visualize the approach of the metal to the olefin as shown below (left), it is clear that two new chiral centers (*S*,*S*) or (*R*,*R*) are generated, depending on the side of the olefin used for bond formation. Thus, a racemic solution is expected from the reaction with fumaric acid and a *meso* compound from the reaction with maleic acid (below, right). The crystallographic characteristics of **ix** were given by these authors [18], who described the space group as $C222_1$ – an enantiomorphic one, implying the substance crystallizes as a conglomerate.





The structure described for **ix** contains an octahedrally coordinated Ru(II) ion with an undissociated, π-bonded fumaric acid [18] occupying the sixth octahedral site



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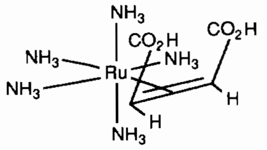

x

Figure 4 of Ludi's paper [18] shows a pair of *trans*-disposed -CO_2H groups which are ideally oriented to form hydrogen bonds between the carboxylate O1 and the hydrogens of the terminal $-NH_2$ groups. As in the case of [*cis*-$Co(en)_2(NO_2)_2$] cations, this Ru(II) species has axial (C_2) symmetry, which in this case is crystallographically demanded [18]; on the other hand, the isomer derived from maleic acid (see **x**, above right) has mirror symmetry.

In previous discussions, we noted [7] that flexible molecular ensembles, capable of acquiring conformations with symmetry elements higher than axial seem, almost invariably, to display them in the solid state while crystallizing in racemic form; or so it seems for the species sampled in our earlier survey [7]. If this principle is general, and the -NH_3 ligands are not fixed into arrays stable enough to impart dissymmetry to the cation, it is expected that, unlike the fumarate, the maleate will crystallize as a racemate.

Conclusions

New classes of widely different compounds, sharing specific stereochemical features detailed earlier [1–7], have been found, as suspected, to share the property of having a high propensity for conglomerate crystallization; thus, it no longer seems the initial observations were the property of a class of substances, narrow enough in nature as to render them as oddities of a limited sample.

Acknowledgements

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