

1,2-Dithiolane-3-carboxylic acid. The crude mercapto-acid was neutralized with 1 000 ml of dilute sodium-bicarbonate solution, and 2 ml 1 % ferric chloride was added, resulting in a solution of deep blue colour. With mechanical stirring and cooling with ice, 30 % hydrogen peroxide was added until the blue colour disappeared. The solution was acidified with sulfuric acid and extracted with benzene. (Part of the product was insoluble in benzene, but could be extracted with ether.) The benzene solution was dried and distilled. The crystallized residue weighed 5 g (15 % calculated on methyl α,γ -di-thiolacetoxy-butyrates). Recrystallization from cyclohexane-benzol gave very pale yellow crystals m. p. 81–82°. (Found: Eq. wt. 150.6; S 42.61; Mol. wt. 147. Calc. for $C_4H_6O_2S_2$: Eq. wt. 150.2; S 42.69; Mol. wt. 150.2.) The molecular weight was determined ebullioscopically in acetone. From the acetone solution the acid was recovered as large crystals m. p. 147°.

Oxidation with gaseous oxygen using ferric chloride as catalyst and oxidation with iodine gave about the same yield as the peroxide oxidation.

Reduction. The polymeric acid was almost quantitatively reduced to the mercapto-acid with zinc powder¹. (Titr. with NaOH and I_2 gave: Eq. wt. 152.8 and 160.1; Calc. for $C_4H_6O_2S_2$: Eq. wt. 152.2.)

Preliminary experiments on resolution. 0.15 g (0.001 mole) of rac. 1,2-dithiolane-3-carboxylic acid and 0.29 g (0.001 mole) of cinchonidine were dissolved in 2 ml ethanol and 1 ml water was added. Crystallization overnight yielded 0.20 g of salt. The acid was liberated from its salt in the usual manner. The rotatory power was measured in alcohol. M. p. 60–62°.

$$[\alpha]_D^{25} = +158^\circ$$

Preliminary value of the dissociation constant. In a solution of 1.090×10^{-4} moles of 1,2-dithiolane-3-carboxylic acid and 1.090×10^{-4} moles of its sodium salt in 15 ml water the pH was found to be 3.42.

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Crystal Field Stabilization of First Transition Group Complexes

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The crystal field of Bethe¹ has been applied to the first transition group by Ilse and Hartmann², Santen and Wieringen³ and Orgel⁴. Ballhausen and the present authors⁵⁻⁸ have extended these applications, and in this communication special attention will be drawn to the energy decrease due to crystal field perturbations on complex ions with an unfilled 3d-shell.

Table 1 gives the data for crystal fields with cubic symmetry (originating from octahedral and tetrahedral complexes). In the cases where the complexes with different total spin quantum number are known, also the lowest value of S observed in complexes is considered. The stabilization parameter is defined: $\rho = 2a - 3b$, where a is the number of γ_5 - and b the number of γ_3 -electrons in a strong crystal field of cubic symmetry^{9,10}. The two states γ_5 and γ_3 of one d-electron have the energies E_2 and E_1 respectively². The energy difference $(E_1 - E_2)$ in tetrahedral complexes⁵ equals $-\frac{4}{9}(E_1 - E_2)$ in octahedral complexes. Thus, the tetrahedral configuration gives much lower crystal field influences than the corresponding octahedral configuration. The energy of the groundstate in terms of ρ is decreased by $\frac{\rho}{5}(E_1 - E_2)$ relative to a similar ion of spherical symmetry, *i. e.* a closed shell with $L = 0$. Since $(E_1 - E_2)$ in octahedral complexes in the first transition group is of the order of magnitude⁶ $10\,000\text{ cm}^{-1}$

Table 1. Stabilization of ground-states in strong crystal fields of cubic symmetry.

Electron number	Examples	Total spin S	Octahedral complexes		Tetrahedral complexes	
			Stabilization parameter ρ	Orbital degeneracy e	Stabilization parameter $-\rho$	Orbital degeneracy e
d^0	Ca ⁺⁺ , Sc ⁺⁺⁺	0	0	1	0	1
d^1	Ti ⁺⁺⁺	$\frac{1}{2}$	2	3	3	2
d^2	V ⁺⁺⁺	1	4	3	6	1
d^3	V ⁺⁺ , Cr ⁺⁺⁺	$\frac{3}{2}$	6	1	4	3
d^4	Cr ⁺⁺ , Mn ⁺⁺⁺	2	3	2	2	3
		1	8	3	7	3
d^5	Mn ⁺⁺ , Fe ⁺⁺⁺	$\frac{5}{2}$	0	1	0	1
		$\frac{1}{2}$	10	3	10	3
d^6	Fe ⁺⁺ , Co ⁺⁺⁺	2	2	3	3	2
		0	12	1	8	
d^7	Co ⁺⁺	$\frac{3}{2}$	4	3	6	1
		$\frac{1}{2}$	9	2	6	
d^8	Ni ⁺⁺	1	6	1	4	3
		0	6	2	4	3
d^9	Cu ⁺⁺	$\frac{1}{2}$	3	2	2	3
d^{10}	Zn ⁺⁺ , Ga ⁺⁺⁺	0	0	1	0	1

(= 28 kcal/mole) with divalent ions and 20 000 cm⁻¹ with trivalent ions, this stabilization energy can be considerable⁴ even though it must be subtracted from the energy of the (often intermixed) excited states of the free ion in the magnetically anomalous complexes.

Another feature of the stabilization first mentioned by Orgel⁴ will be discussed in this note: The preference for γ_6 -electrons in the octahedral complexes corresponds to high electron densities in the eight directions¹ between the ligands, while the missing γ_8 -electrons are directed towards the six ligands. Thus, the electrostatic potential near the ligands will be higher than corresponding to the external charge of the complex, *e.g.* in diamagnetic cobalt(III) complexes, the effective external charge might be expected to vary between +9 in the direction of the ligands and -3 between the ligands. But a closer electrostatic calculation shows that the screening is not only determined by the number of d-electrons situated directly between the ligand and the cobalt(III) nucleus. Actually, only a variation between +4 and +2 can be present. Nevertheless, the result supports the idea that complexes like [Co(NH₃)₆]⁺⁺⁺ can be held together by electrostatic forces.

The current theories⁹ on covalency in coordination compounds assume donation of twelve electrons from the ligands to the central ion in octahedral complexes, forming hybridizations of the d^2sp^3 -type. It does not seem accidental that precisely the two empty γ_8 -orbitals are used for this operation. The deviation from the spherical symmetry of the d-shell (*i.e.* $\rho \neq 0$) corresponds to a preferred location of ligands in the directions of the empty γ_8 -orbitals, which are the spherically symmetric complement to the filled γ_6 -orbitals. In the authors' opinion, it does not seem necessary to explain the electrostatic energy decrease by further addition of electron-pair formation of donated character. The tetrahedral sp^3 -hybridizations, which are said to occur in ions with no crystal field perturbations, constitute as peculiar a hypothesis in coordination chemistry. While the explanation of chemical bonding between four hydrogen atoms each with one un-paired electron and a carbon atom with four un-paired electrons is so successful, the similar treatment of zinc(II) or beryllium(II) complexes does not easily compete with the electrostatic picture according to Fajans¹⁰.

In Table 1, the orbital degeneracy e is also given for all the groundstates except

when it cannot be certainly predicted from atomic spectroscopy. Only in the cases for which $e = 1$ are the complexes stable¹¹ for crystal fields of purely cubic symmetry. For other e values the crystal fields must be somewhat distorted; for $e = 2$, to tetragonal, and for $e = 3$, to rhombic or tetragonal symmetry. Crystal field calculations explain easily^{5,7} the occurrence of tetragonal symmetry in copper(II) or in diamagnetic nickel(II) complexes with no need of dsp^3 -hybridization. If complexes are classified according to $e = 1$ and $e = 2$ or 3 , it is interesting to compare the absorption spectra as well as the consecutive complexity constants in the various cases. Thus displacements of bands towards lower wavenumbers by increasing symmetry of the crystal field are found only in systems with $e > 1$ (e.g. in the cupric ammonia system) and irregularities in the rest effects are found e.g. to a higher degree in the cobalt(II) ammonia system than in the nickel(II) system^{12,p.57}.

The activation energies are high only when $\rho(E_1 - E_2)$ is large and $e = 1$. Bjerrum and Poulsen¹³ found empirically that half-completed and completed d-shells (with $\rho = 0$) and nearly complete d-shells (with $e > 1$) give low activation energies, which increase with the oxidation state for purely electrostatic reasons, just as do the complexity constants. In the robust complexes (e.g. $\rho = 6$ and $e = 1$ in chromium(III) and nickel(II)) the activation energy increases with the value of $(E_1 - E_2)$, which⁶ is $17\,400\text{ cm}^{-1}$ in $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ and $7\,600\text{ cm}^{-1}$ in $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$. If the magnetism is changed during a consecutive complex formation, a sudden change of activation energies and complexity constants are expected, as found in the cyanide and α,α' -dipyridyl complexes of iron(II)¹⁴. Magnetically anomalous, octahedral complexes should only be possible when $\frac{2}{5}(E_1 - E_2)$ is larger than the energy of the excited states in the free ion with low S , and they are mainly restricted to the electron configurations d^5 and d^6 with the highest value of ρ . These facts will be discussed in the following papers of the series "Studies of Absorption Spectra"¹⁵.

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Note on the Structure of Dimethoxydihydrofurfural Diacetate

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By the action of bromine in methanol on furfural diacetate Clauson-Kaas and Fakstorp¹ obtained an 81% yield of an oily dimethoxydihydrofurfural diacetate which by hydrolysis and oxidation with periodic acid gave *cis*- β -formylacrylic acid. Therefore the product must be a derivative of 2-pentene-1,5-dial-4-one (II) and it was assumed to have structure I in analogy with other dimethoxydihydrofurans.

When repeating the synthesis of dimethoxydihydrofurfural diacetate a somewhat lower yield (about 65%) was regularly obtained while the reaction product at the same time contained about 15% of unreacted furfural diacetate. Since the methoxylation of furfural diacetate is a slower reaction than the usual furan methoxylation reactions, the discrepancy may be due to a catalytic effect.