

The Necessity of Chelation for the Cotton Effect of the *d-d* Transitions in Inorganic Complexes

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Djerassi and Geller¹ have shown by optical rotatory dispersion measurements that aliphatic carbonyl compounds of the types, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_n\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_n\text{COCH}_3$, show the Cotton effect in the 3000 Å carbonyl transition even if n is 2 or 3. Thus, the asymmetric centre in such compounds influences the chromophore even when they are separated by several atoms.

We have measured the circular dichroism (CD) of some inorganic transition metal complexes containing optically active ligands. It has been found that for complexes of the unidentate ligands, *d*-2-aminobutane and *d*- α -methylbutyrate, no CD was detectable, although, by analogy to above, it might be expected. Therefore, in these complexes, the influence of the asymmetric carbon on the chromophore must be much smaller than for the carbonyls.

Solutions of copper(II) and equal amounts of *d*- α -methylbutyric acid and sodium *d*- α -methylbutyrate were examined for CD, but in vain. Further, copper(II) and *d*-2-aminobutane solutions containing mostly copper(II) as tetrakis(*d*-2-aminobutane)copper(II) showed no CD in the range 8000–2200 Å. The robust complexes *trans*-bis(*d*- α -methylbutyrate)tetramminecobalt(III) and *d*- α -methylbutyratepentaamminecobalt(III) were prepared and were found to exhibit no detectable CD.

The asymmetric centre is closer to the chromophore when the donor atom itself is asymmetric. Due to experimental difficulties very few attempts to prepare such compounds with unidentates have been described. Ingold *et al.*² have prepared the *d*-2-butylmercury(II) ion, which forms complexes with ligands such as halides, pseudo halides and 8-quinolinolate. Preliminary investigations³ with complexes of this kind have not resulted in observable CD in the range above 2200 Å. No experiments have yet been reported where there has been complex formation with unidentate ligands containing an asymmetric

nitrogen, phosphorus, arsenic, or sulphur atom as donor.

It has long been known that some optically active ligands, *e.g.* *d*-tartrate ions and *l*-propylenediamine (*l*-pn), form complexes with the transition metal ions, which are optically active in the *d-d* transitions.⁴ Therefore, we propose tentatively that an induced Cotton effect in a *d-d* transition of a transition metal complex will only be of measurable magnitude if the asymmetric ligand is a chelate. Further studies are being carried out to test the generality of this rule.

Such an empirical rule may be of great value in the determination of coordinate species in solutions. As an example we will discuss the complexes of copper(II) and (+)lactate (in the following L = (+)lactate).

Fronæus⁵ has measured the stability constants for the complex formation between copper(II) and acetate as well as glycollate ions.

The successive formation constants in a 1 M NaClO₄ medium and at 20° are given in Table 1.

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	pK_a
Acetate	1.67	0.98	0.42	-0.19	4.61
Glycollate	2.34	1.36	0.29	-0.22	3.63

If glycollate was to act as an unidentate ligand, one would expect $\log K_1$ and $\log K_2$ for glycollate to be less than those for acetate because the pK_a of glycollic acid is about 1 logarithmic unit less than that of acetic acid. The fact that the glycollate complexes are more stable strongly suggests that glycollate acts as a chelate.

Cannon and Kibrick⁶ have shown that the stability of 1:1 glycollate complexes with Zn, Mg, Ca, Sr, and Ba are identical within experimental uncertainty with the stability of the 1:1 lactate complexes of the same metals. We have used Fronæus' data for the copper(II) glycollate system to calculate the concentrations of the various copper(II)-lactate complexes for the solutions given in Table 2. For the higher complexes the probable error amounts to 10–20 %, and the calculated concentrations are only meant to give a rough idea of the species present. The measured CD at 7000 Å is also given in Table 2. The recorder deflections on the dichrograph were not more than 6–12 mm corresponding to $(\epsilon_1 - \epsilon_2)$ for the 1:1 and 1:2 complexes of about 0.03 and 0.06 density units.

Table 2. Distribution of copper (II) over the various (+) lactate complexes (calculated by use of Fronæus⁵ stability constants for the glycollate complexes) and the measured circular dichroism.

$$C_{\text{Cu}} = 9.79 \text{ mM}, C_{\text{NaL}} = C_{\text{HL}} = C_{\text{I}}, \text{ and } C_{\text{NaL}} + C_{\text{NaClO}_4} = 1.00 \text{ M.}$$

No.	C_{L}	$[\text{CuL}^+]$	$[\text{CuL}_2]$	$[\text{CuL}_3^-]$	$[\text{CuL}_4^{2-}]$	$\Delta D \times 10^4$ in $d.u$ /5 cm
1	14.55	5.50	1.00	0.01	0.00	9.1 ± 0.5
2	32.41	5.50	2.95	0.13	0.00	13.4 ± 0.5
3	97.3	3.09	5.63	0.87	0.04	18.0 ± 0.5
4	324.1	0.77	5.38	3.16	0.57	14.4 ± 0.5
5	408.0	0.55	4.80	3.55	0.83	10.8 ± 0.5

All the concentrations in mM.

Therefore, there is no hope of doing quantitative experiments on this system. It seems obvious, however, that the Cotton effect in the red copper(II) band is produced by chelate species because the measured CD reaches its maximum when the concentration of the chelate rings is maximum.

The method may be applied quantitatively in the case where the optically active chelates give large Cotton effects in the $d-d$ transitions of the complex. It may be possible in a more direct way to confirm equilibrium constants of the type $K = [\text{M chel}]/[\text{M chel}^*]$, where $[\text{M chel}^*]$ denotes the concentration of the open chain adduct (as discussed by Bjerrum and Larsen⁷) if the usual equilibrium studies are used in conjunction with CD experiments.

The stereochemistry of chelate rings has been discussed for many years. Theilacker⁸ pointed out that a chelate ring such as the metal ethylenediamine ring is non-planar and, as a consequence, must be itself asymmetric. Mathieu⁹ and Corey and Bailar¹⁰ have given a detailed discussion concerning the effects of substitutions in a puckered ring and the interactions between puckered chelate rings in a molecule. Corey and Bailar propose that the bonds from the ligand ring atom contain axial or equatorial character. The reason for the observed Cotton effect in a complex such as mono-*l*-propylenediaminecopper(II)⁴ is probably that the one ring conformation with the methyl group in the equatorial position should dominate over the other conformation where the methyl group must occupy the axial position. This means that the equilibrium ratio between the two

"enantiometric"* ring conformations must be displaced from a 1:1 ratio to a ratio depending on the steric interactions of the substituent in the two conformations. Therefore, as one enantiomer is preferred, it is not surprising that CD is observed.

The fact that copper(II)-(+)-lactate complexes exhibit the Cotton effect indicates therefore, not only that the ligand functions as a chelate, but also that the chelate ring is more or less puckered.

Experimental. Copper (II)-(+)lactate solutions were made from commercial chemicals (Riedel de Haën, p.a.).

The measurements of CD were performed with a Roussel-Jouan Dichrograph with an extended wavelength scale (8000–2200 Å). In the negative attempts we used combinations of cell lengths and concentrations to try to detect CD (the optical density was never more than 2.0 for the absorption band in question). The sensitivity is supposed to be 1.5×10^{-4} d.u. corresponding to 1 mm recorder deflection. The copper (II)-(+)lactate solutions were measured in 5 cm cells.

Preparations. Optically active α -methylbutyric acid was prepared according to Markwald¹¹ from commercial optically active amyl alcohol (Fluka).

Commercial 2-aminobutane (Fluka) was resolved by recrystallization of the *d*-tartrate.¹²

Trans $[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{COO})_2]\text{ClO}_4$, HClO_4 (A) and $[\text{Co}(\text{NH}_3)_5(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{COO})](\text{ClO}_4)_2$, H_2O (B) were prepared by a method similar to that for the corresponding isovaleriato complexes.^{13,14} Analysis for A: Found: NH_3 12.50, Co 11.22. Calc. from the above formula: NH_3 12.88, Co 11.14.

Analysis for B: Found: NH_3 18.42, Co 12.88. Calc. from the above formula: NH_3 18.43, Co 12.75.

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1. Djerassi, C. and Geller, L. E. *J. Am. Chem. Soc.* **81** (1959) 2789.
2. Charman, H. B., Hughes, E. D. and Ingold, C. J. *J. Chem. Soc.* **1959** 2528.
3. Barbieri, R. *et al.* *To be published.*

* The rings are enantiomers with respect to the conformation, but not with respect to the configuration of the asymmetric carbon.

4. Woldbye, F. *Optical Rotatory Dispersion of Transition Metal Complexes*. European Research Office, U. S. Army, Frankfurt a.M. 1959.
5. Fronåus, S. *Komplexsystem hos Koppar*, *Diss.* Lund 1948.
6. Cannan, R. K. and Kibrick, A. *J. Am. Chem. Soc.* **60** (1938) 2314.
7. Bjerrum, J. and Larsen, E. in *Essays in Coordination Chemistry*. Birkhauser Verlag, Basel 1964.
8. Theilacker, W. *Z. anorg. Chem.* **234** (1937) 161.
9. Mathieu, J.-P. *Ann. Phys. Paris* 11. serie **19** (1944) 335.
10. Corey, E. J. and Bailar, J. C. *J. Am. Chem. Soc.* **81** (1959) 2620.
11. Marckwald, W. *Ber.* **37** (1904) 1038.
12. Thomé, L. G. *Ber.* **36** (1903) 582.
13. Lindhard, M. and Weigel, M. *Z. anorg. Chem.* **260** (1949) 65.
14. Lindhard, M. and Rau, B. *Z. anorg. Chem.* **271** (1953) 121.

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Effect of Long Heat-Denaturation of Collagen on Its Electrophoretic Pattern

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For the denaturation of soluble collagen, Piez *et al.*¹ suggested heating at pH 4.8 for 15 min at +40°C. The detailed investigation by Engel² showed that the denaturation proceeds in two stages: the helical structures are lost very rapidly but the separation of the chains takes more time, and he suggested heating for 90 min for complete denaturation. In a later paper Engel and Beier³ demonstrated that the α - and β -components are not stable, but already after 9 h at +40°C in pH 3.7 citrate buffer 10–20 % of the β -component was lost from the sedimentation pattern, and also degradation products of small molecular weight were obtained from both α - and β -fractions. These findings prompted us to check the electrophoretic pattern of heat-denatured collagen after various intervals.

The collagen preparation was obtained from rat tail tendon fibres by extraction for 24 h in the cold with 20 volumes of 3 % (v/v) acetic acid. (The material had been first extracted exhaustively with 0.4 M NaCl, buffered to pH 7.3 with 1/15 M phosphate, and the soluble fraction discarded.) The collagen was precipitated from the acetic acid extract by dialysis against pH 7.3, M/15 phosphate buffer. The precipitate was lyophilized, dissolved in 3 % acetic acid and dialyzed against the pH 4.5 acetate buffer, ionic strength $\mu = 0.022$, which was also used in the preparation of the gel for the electrophoretic run.⁴ For the prevention of microbial growth, the buffer was saturated with octanol. No turbidities were observed. After a preliminary denaturation at +40°C for 15 min, the sample was divided in separate lots, which were kept at +4°C, until they

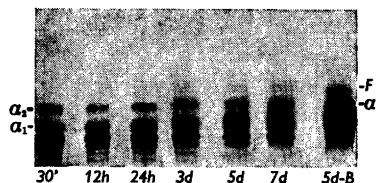


Fig. 1. Effect of long heat-denaturation of soluble collagen on the starch gel electrophoretic pattern. The duration of the denaturation at +40°C is indicated. The sample size was 400 μ g, but in some runs larger samples were applied to accentuate the fast-moving fraction F (the pattern to the extreme right).

were immersed in a +40°C water bath at appropriate intervals to get the indicated heating times at the beginning of the simultaneous electrophoretic runs on the same gel sheet (Fig. 1, except the run marked 5 d-B.).

The pattern does not change essentially in a week, but three observations were made: (1) The slow-migrating fractions were gradually lost during the heating and they therefore represent larger complexes, which are broken down. (2) The α_1 -fraction becomes rather broad. The separation to subcomponents is not clear, but on the basis of unpublished work by V. Nántö from our laboratory we believe that this fraction is not homogeneous. (3) After about 3 days there appears a new distinct band designated F, which migrates faster than the α_2 -component. In Fig. 1 the