No attempt has been made to eliminate the influence of Fe(III) as in the case of the thiocyanate method.

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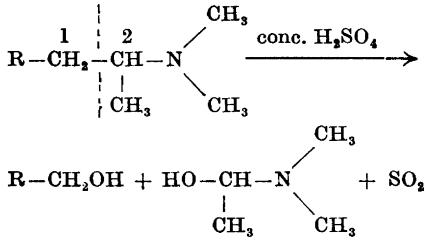
Correction to "Formation of Free Radicals from Some Phenothiazine Derivatives as Studied by Electron Spin Resonance" *

CARL LAGERCRANTZ

Department of Medical Physics, University of Göteborg, Sweden

In the reaction scheme on p. 1554 the side chain of the promethazine molecule is erroneously given as 3-dimethylamino-2-methyl-propyl. This is corrected to 2-dimethylaminopropyl and the products obtained in the reaction with conc. sulphuric acid are 10-(hydroxymethyl)-phenothiazine, 1-dimethylaminoethanol and sulphur dioxide.



R = phenothiazine nucleus.

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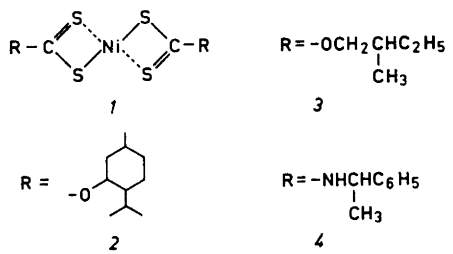
Optical Rotatory Dispersion of some Nickel Complexes

BERNDT SJÖBERG * and ROLF BACKSTRÖM

Department of Organic Chemistry, Chemical Institute, University of Uppsala, Uppsala, Sweden

In a recent investigation [1] of xanthates it was shown that these compounds often exhibit strong Cotton effects and that the anomalous dispersion curves can be used for stereochemical correlations. However, the amplitudes and at times even the appearance of Cotton effects of xanthates are very dependent upon chemical constitution. Thus rigid compounds, like bornyl xanthates, have Cotton effects of large amplitudes whereas the methyl xanthate of 2-methylbutanol only shows a plain dispersion curve. We thought it possible to increase the interaction between the C=S chromophore and the various substituents of the pertinent molecule by complexing with a metal.

In the preparation of alkyl xanthates the appropriate alcohol is first treated with alkali and carbon disulfide and then with an alkyl halide. If nickel acetate is added instead of the alkyl halide, a coloured metal complex *1* precipitates. Drawert, Reuther and Born [2] recently investigated this type of complex of several racemic alcohols and found a series of absorption bands in the visible and ultraviolet region. The first group of bands are situated at about 480 and 420 mμ, and the extinction of the complexes seems to be fairly dependent on the structure of the alcohol. However, the ε values will generally be of the order of



1 *3*

2 *4*

* Present address: AB Astra, Södertälje, Sweden.

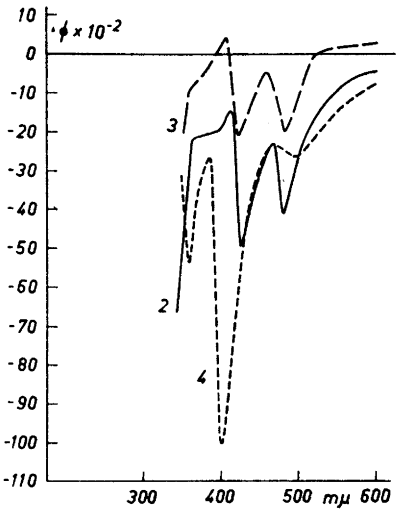


Fig. 1. Optical rotatory dispersion curves of bis[(—)-menthylxanthate]nickel(II) (*2*) bis[(+)-2-methylbutylxanthate)-nickel(II) (*3*) and bis[(—)-α-phenylethyldithiocarbamate)-nickel (II) (*4*).

500—1 000 and 1 000—2 000, respectively. Such high ε values will not allow convenient rotatory dispersion measurements through the absorption region unless the amplitudes of the Cotton effects are large. In order to see if metal complexes related to structure *1* are suitable for rotatory dispersion studies we have prepared this type of nickel complexes from optically active alcohols.

The compounds *2* and *3* prepared from menthol and 2-methylbutanol, respectively, have both absorption bands at 477 and 417 mμ (log ε ~ 3.1 and 3.3); rotatory dispersion curves in Fig. 1. The complex *2*, derived from menthol, has two negative Cotton effects of fairly large amplitudes corresponding to the 477 and 417 mμ bands. But most important the nickel complex *3* prepared from 2-methylbutanol, also exhibits Cotton effects related to the two absorption bands. In this way it seems possible to circumvent the previously mentioned difficulty with rotatory dispersion studies of simple alcohols whose xanthates will not exhibit anomalous dispersion curves.

Optical rotatory dispersion curves of dithiocarbamates have been shown [1,3] to be similar to those of the corresponding xanthates. For that reason we also included amines in our present studies, for example the nickel complex *4* prepared from optically active α-phenylethylamine. This complex has absorption bands at 480 and 385 mμ (log ε ~ 2.3 and 3.6), and strong Cotton effects are found in the rotatory dispersion curve (Fig. 1).

Applications of metal complexes (nickel, copper, etc.) in stereochemical studies of alcohols and amines will be discussed further in our full papers.

Experimental. The bis[xanthate]nickel(II) complexes *2* and *3* were prepared according to the method used on racemic alcohols by Drawert, Reuther and Born [2], and bis[dithiocarbamate]-nickel(II) (4) according to a similar procedure reported by Losanitsch [4].

Bis[(—)-menthylxanthate]nickel(II) (2), m.p. 176°d, λ_{max} dioxane 477 (log ε = 3.08) and 417 mμ (log ε = 3.32). (Found: Ni 11.27. $C_{22}H_{38}O_2S_4Ni$ requires Ni 11.25).

R.D. (Fig. 1), *c*, 0.023 in dioxane: Φ_{589} −450°, Φ_{480} −4 130°, Φ_{467} −2 270°, Φ_{426} −4 990°, Φ_{413} −1 450°, Φ_{345} −6 700°.

Bis[(+)-2-methylbutylxanthate]nickel(II) (3), m.p. 80—84°d., λ_{max} dioxane 477 (log ε = 3.03) and 417 mμ (log ε = 3.32). (Found: Ni 16.81; $C_{12}H_{22}O_2S_4Ni$ requires 15.23).

R.D. (Fig. 1), *c*, 0.021 in dioxane: Φ_{589} + 250°, Φ_{483} −2 020°, Φ_{462} −440°; *c*, 0.011: Φ_{421} −2 130°, Φ_{406} + 440°, Φ_{350} −2 200°.

Bis[(—)-α-phenylethyldithiocarbamate]nickel (II) (4), m.p. 67°d. λ_{max} methanol 480 (log ε = 2.29) and 385 mμ (log ε = 3.62). (Found: Ni 12.89; $C_{18}H_{20}N_2S_4Ni$ requires 12.24).

R.D .(Fig. 1) *c*, 0.020 in methanol: Φ_{589} −880°, Φ_{493} −2 650°, Φ_{464} −2 340°; *c*, 0.010: Φ_{400} −10 100°, Φ_{384} −2 650°, Φ_{359} −5 300°, Φ_{350} −3 180°.

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