SHORT COMMUNICATIONS

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

We wish to thank the Swedish Atomic Energy Company for financial support and for permission to publish this method. We are also indebted to Professor Lars Gunnar Sillén and Docent Sten Ahlrand for some helpful comments and to Dr. Derek Lewis for English text revision.


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Optical Rotatory Dispersion of some Nickel Complexes
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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. Drewert, 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 mp, and the extinction of the complexes seems to be fairly dependent on the structure of the alcohol. However, the e values will generally be of the order of

\[
\begin{align*}
R - CH_2 - CH - N & \quad + \quad SO_2 \\
R - CH_2OH & \quad + \quad HO - CH - N & \quad + \quad SO_2 \\
R = & \quad \text{phenothiazine nucleus.}
\end{align*}
\]


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

\[
\begin{align*}
1 & \quad 2 \\
R - CH_2 & \quad CH - N & \quad + \quad SO_2 \\
R - CH_2OH & \quad + \quad HO - CH - N & \quad + \quad SO_2 \\
R = & \quad \text{phenothiazine nucleus.}
\end{align*}
\]

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Optical rotatory dispersion curves of dithiocarbamates have been shown 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 prepared from optically active α-phenylethylamine. This complex has absorption bands at 480 and 385 μ (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, and bis[dithiocarbamate]-nickel(II) (4) according to a similar procedure reported by Losanitsch.

Bis(--)menthylxanthate]nickel(II) (2), m.p. 170°d, λmax dioxane 477 (log ε = 3.08) and 417 μ (log ε = 3.32). (Found: Ni 11.27, C15H30O3S2Ni requires Ni 11.25).

R.D. (Fig. 1), c. 0.023 in dioxane, Φ385 = 450°, Φ417 = 4.130°, Φ437 = 2.270°, Φ465 = 4.990°, Φ513 = 1.450°, Φ545 = 6.700°.

Bis(--) menthylxanthate]nickel(II) (3), m.p. 80–84°d, λmax dioxane 477 (log ε = 3.03) and 417 μ (log ε = 3.32). (Found: Ni 16.81; C15H30O3S2Ni requires 15.23).

R.D. (Fig. 1), c. 0.021 in dioxane: Φ385 + 250°, Φ417 = 2.020°, Φ437 = 4.400°; c. 0.011: Φ385 = 2.130°, Φ400 = 4.400°, Φ465 = 2.000°.

Bis(--) α-phenylethylxanthate]nickel(II) (4), m.p. 67°d, λmax methanol 480 (log ε = 2.29) and 385 μ (log ε = 3.62).

(Found: Ni 12.89; C16H36N2S2Ni requires 12.24).

R.D. (Fig. 1), c. 0.020 in methanol: Φ385 > 880°, Φ437 > 2.650°, Φ465 = 2.340°; c. 0.010: Φ400 = 10.100°, Φ385 = 2.650°, Φ350 > 5.300°, Φ325 > 3.180°.

4. Losanitsch, S. M. Ber. 24 (1891) 3026.

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