[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Dipole Moments of Some Ni(II) Mercapto-Ester Chelates

BY JOHN J. DRANEY, JR., AND MICHAEL CEFOLA

RECEIVED AUGUST 28, 1953

The bis-ester nickel chelates of ethyl thioglycolate, hexadecyl thioglycolate and ethyl thioacetoacetate have been prepared. The apparent dipole moments of these chelates obtained from measurements in dilute benzene solutions at 25° are 2.4, 2.6 and 4.5 *D*, respectively. On the basis of these moments and the observed diamagnetism in the thioglycolic acid ester chelates, the molecules are shown to possess a planar distribution of the coördinating centers about the nickel atom and rotation of the alkoxy groups with respect to the plane of the chelate ring. The nickel chelate of ethyl thioacetoacetate is unique in being able to form a stable dipyridine derivative.

Introduction

As a continuation of a study of sulfur-containing chelates[1] the dipole moments of bis-(hexadecylthioglycolato)-nickel, bis-(ethylthioglycolato)-nickel and bis-(ethylthioacetoacetato)-nickel have been obtained. Chelates of nickel were studied because of their stability, solubility in benzene and the greater ease of interpreting data for a tetracovalent central ion than that pertaining to a hexacovalent ion.

Experimental Procedure

Dipole moments were determined with a heterodyne beat apparatus described elsewhere[1] and using the same procedure.

The benzene used was E. and A. Tested Purity, crystallized, dried over sodium wire several days, refluxed over P_2O_5 for a few hours and then distilled over P_2O_5 through an all-glass apparatus containing a 90-cm. Vigreux column.

The magnetic measurements were obtained by the Gouy method. The sample tube was of the double-ended, two-compartment type, the lower one being evacuated. The entire tube was 20 cm. long and had an inside diameter of 4 mm. Solid reagent grade ferrous ammonium sulfate was used as the calibrating agent. Measurements were made at 23°.

Solutes. Bis-(ethylthioglycolato)-nickel.—The original procedure of Drummond and Gibson[2] has been modified as follows. To a solution of 12.11 g. of nickel nitrate and 6.1 g. of sodium acetate in 150 ml. of 10% ethanol is added, with rapid stirring, 10.00 g. of ethyl thioglycolate dissolved in 10.0 ml. of ethanol. The dark red brown complex[3] precipitates immediately as a viscous mass. The entire mixture is extracted several times with chloroform, washed thoroughly with water, dried over sodium sulfate, treated with norite and evaporated on the steam-bath to just short of dryness, recrystallized twice from ethanol, dried *in vacuo* over sulfuric acid, to dark red, nearly black, crystals, m.p. 104–105°. It is soluble in benzene, chloroform, dioxane, acetone, ether, ethyl acetate, carbon tetrachloride and carbon disulfide, insoluble in both ethanol and amyl alcohol.

Anal. Calcd. for $Ni(SCH_2COOC_2H_5)_2$: C, 32.3; H, 4.8; Ni, 19.8. Found: C, 32.6; H, 4.7; Ni, 19.8.

Bis-(hexadecylthioglycolato)-nickel.—4.59 g. of KOH in 25 ml. of 50% ethanol is added to a suspension of 25.32 g. of hexadecyl thioglycolate and 11.64 g. of nickel nitrate in 200 ml. of 50% ethanol. The dark brown precipitate is decanted several times with 50% ethanol, filtered and pressed dry between filter paper, dissolved in cold chloroform, dried over sodium sulfate, treated with norite and evaporated to dryness, care being taken that the actual drying does not take place above 65–70°, recrystallized from absolute ether, dried *in vacuo* over sulfuric acid, giving very small brown red crystals, m.p. 75.5–76.5°. It is soluble in benzene, chloroform, carbon tetrachloride and carbon disulfide, insoluble in dioxane, acetone, ether, ethyl acetate, ethanol and amyl alcohol.

Anal. Calcd. for $Ni(SCH_2COOC_{16}H_{33})_2$: C, 62.7; H, 10.2; Ni, 8.5. Found: C, 62.3; H, 10.1; Ni, 8.5.

Bis-(ethylthioacetoacetato)-nickel can be obtained by direct combination of ester and nickel salt as in previous examples or by loss of pyridine from dipyridine complex. The latter is accomplished by heating the dipyridine compound to 75–80° for several hours, recrystallizing from absolute methanol, and drying *in vacuo* over sulfuric acid to give fine brown needles, m.p. 110–111.5°.

Anal. Calcd. for $Ni(CH_3CSCHCOOC_2H_5)_2$: C, 41.3; H, 5.2. Found: C, 41.8; H, 5.3.

Bis-(ethylthioacetoacetato)-dipyridine-Nickel.—14.60 g. of thioacetoacetic ester dissolved in 10 ml. ethanol is poured into 10 ml. of ethanol containing 5.82 g. of nickel nitrate. The resulting brown solution is poured into 30 ml. of pyridine, turning apple green, and depositing a dense crop of fine crystals of this same color. It was filtered, washed with pyridine and dried in air, yield 8.80 g. It is soluble in ethanol to give a brown solution. Recrystallization from ethanol can be accomplished with only a small amount of the depyridinated solid contaminating the product.

Anal. Calcd. for $Ni(CH_3CSCHCOOC_2H_5)_2(C_5H_5N)_2$: C, 52.1; H, 5.6; Ni, 11.6; N, 5.5. Found: C, 52.1; H, 5.5; Ni, 11.7; N, 5.1.

Bis-(methylthiosalicylato)-nickel.—Dissolve 2.91 g. of nickel nitrate in about 40 ml. of water which contains 1.5 g. of sodium acetate. This solution was shaken with about 40 ml. of chloroform, containing 3.36 g. of methyl thiosalicylate. The dark brown chloroform layer was removed, the solution washed with water, dried over sodium sulfate and treated with norite. Upon evaporating the solution under vacuum, fine brown crystals separated; they were filtered and washed with ether, dried *in vacuo* over sulfuric acid, m.p. 206°.

Anal. Calcd. for $Ni(C_8H_7O_2S)_2$: C, 48.9; H, 3.6. Found: C, 48.8; H, 3.3.

Results

Treatment of data and use of symbols is the same as that previously employed.[1] Data and results are given in Table I. In order to check the precision of the moments found, two separate batches of bis-(hexadecylthioglycolato)-nickel were prepared and solutions prepared from each, using two different batches of benzene. The moments calculated from data obtained in the same concentration range were 2.53 and 2.63 *D*. All moments, therefore, should be regarded as being no more reliable than ±0.1 *D*.

TABLE I

E_1	α	V_1	β	P_2	P_1	μ, Debye
Bis-(hexadecylthioglycolato)-nickel						
Sample 1						
2.270	6.90	1.1448	−1.39	304.1	26.60	2.63
Sample 2						
2.278	6.37	1.1451	−1.57	292.8	26.72	2.53
Bis-(ethylthioglycolato)-nickel						
2.263	7.26	1.1453	−1.83	165.7	26.51	2.38
Bis-(ethylthioacetoacetato)-nickel						
2.274	27.95	1.1452	−1.74	489.3	26.66	4.54

---

[1] C. F. Ferraro, J. J. Draney and M. Cefola, THIS JOURNAL, **75**, 1206 (1953).

[2] A. Drummond and D. Gibson, *J. Chem. Soc.*, 3073 (1926).

[3] No implication regarding structure is attached to the word "complex," used throughout the remainder of this paper.

Due to the intense color of the solutions P_D was calculated from bond refractivities, the refraction of the metal containing bonds being neglected.

Moments at 25° were calculated, using the relationship

$$\mu = 0.221\sqrt{{}_{\infty}P_2 - P_D}$$

The nickel chelates of ethyl and hexadecyl thioglycolate were found to be diamagnetic in the solid state. The latter compound also was found to be diamagnetic in benzene.

Solid bis-(ethylthioacetoacetato)-dipyridine-nickel is paramagnetic with the following characteristics: gram susceptibility = 4.14 × 10^{-6}; atom molar susceptibility = 2353 × 10^{-6}; effective moment in Bohr magnetons = 2.4.

Discussion

All the complexes except that containing pyridine are some shade of red or brown and, since these colors have been associated with diamagnetic nickel,[4] this might be considered as evidence of a planar configuration. Although in 1940 there was only one exception to this rule,[5] it was concluded a few years later[6] that little reliance can be placed on relation of magnetic type to color.

Lack of sufficient examples prohibits any generalizations being made concerning the relationship between configuration and nature of the coördinated groups, but if chelate rings do exist in these molecules, nickel will be surrounded by two oxygen and two sulfur atoms. Bis-(ethylene-bis-thioglycolato)-nickel, in which the same condition exists, is paramagnetic and presumably tetrahedral.[5]

Magnetic susceptibility measurements in themselves do not establish the presence of a chelate ring of the type in Fig. 1a in these compounds, since even the simple mercaptides $Ni(SR)_2$ have been found to be diamagnetic,[7] and therefore polynuclear (Fig. 2 top).

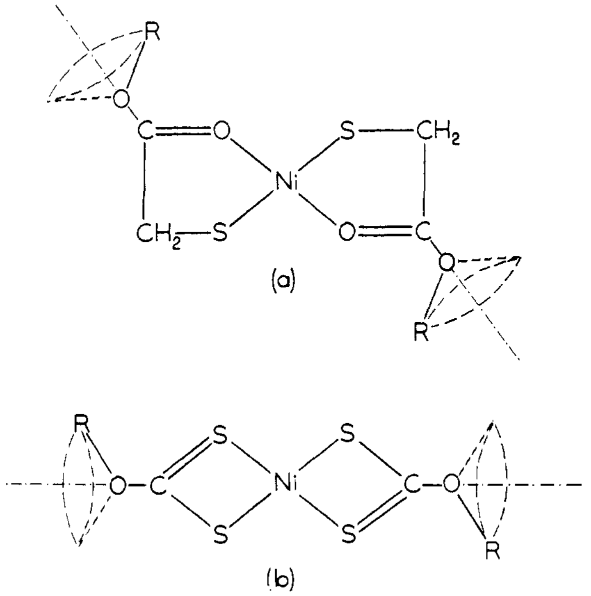


Fig. 1.

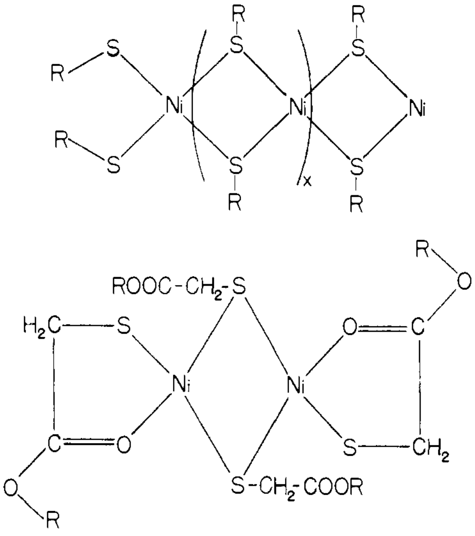


Fig. 2.

The diamagnetism of the solid ethyl and hexadecyl thioglycolate chelates demonstrates the planar configuration about the nickel atom. To eliminate the possibility of a transformation to a tetrahedral configuration upon dissolution, the benzene solution of the hexadecyl chelate was examined and this too found to be diamagnetic. Unfortunately, sufficient material was not available for magnetic studies of the ethyl thioacetoacetato complex.

Attempts were made to prepare pyridine derivatives of all these compounds, and it was found that although under none of the conditions employed could pyridinated compounds of the thioglycolates be obtained, it was simple to prepare a stable dipyridine compound of bis-(ethylthioacetoacetato)-nickel. In this connection, it should be noted that Willis and Mellor[8] have reported difficulty in preparing pyridine derivatives of diamagnetic compounds of nickel, including the xanthate.

The tendency to acquire additional donor groups has been observed for tetrahedral nickel compounds[9] and in the case of bis-(ethylthioacetoacetato)-nickel might in itself be taken as some indication of this configuration.

Bis - (ethylthioacetoacetato) - dipyridine-nickel was found to be paramagnetic (X_M = +2353 × 10^{-6}) and therefore indicative of the octahedral configuration one would expect. The fact that the magnetic moment of this compound (2.4 B.M.) is much less than the theoretical value (2.83) is difficult to explain. However, Willis and Mellor[8] found that a number of chelates of nickel which are diamagnetic in the solid state are paramagnetic in pyridine and some other organic solvents, the moments ranging from 0.8 to 3.32 B.M. and several having moments of 2.2 to 2.5 B.M.

Finn, Hampson and Sutton[10] have shown that several of the metal chelates of acetylacetone have

---

(4) R. S. Nyholm, *Quart. Rev. (London)*, **3**, 321 (1947).

(5) D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. W.*, **74**, 475 (1940).

(6) H. A. McKenzie, D. P. Mellor, J. E. Mills and L. W. Short, *ibid.*, **78**, 70 (1944).

(7) K. A. Jensen, *Z. anorg. Chem.*, **252**, 227 (1944).

(8) J. B. Willis and D. P. Mellor, THIS JOURNAL, **69**, 1237 (1947).

(9) F. P. Dwyer and D. P. Mellor, *ibid.*, **63**, 81 (1941).

(10) H. F. Finn, G. C. Hampson and L. E. Sutton, *J. Chem. Soc.*, 1259 (1938).

unusually large atom polarizations, reaching a value as high as 60% of the electron polarization. In like manner, the observed apparent moments of bis-(8-hydroxyquinolino)-lead and bis-(disalicylidenemethylamino)-copper have also been attributed by Charles and Freiser[11] to an abnormally large atom polarization.

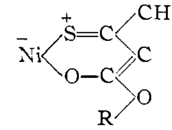
Due to this uncertainty in atom polarization, it is usually impossible to say whether compounds of the type now under consideration are either polar or non-polar when the moments are small. In the case of the chelates of ethyl and hexadecyl thioglycolate, it is safe to conclude that the molecules have a real moment. Thus, with bis-(ethylthioglycolato)-nickel, even when the atom polarization is taken to be 100% of the electron polarization, the moment does not become negligible, showing the molecule to possess a real moment.

Although the apparent moments of the ethyl and hexadecyl thioglycolate chelates are 2.4 ± 0.1 *D* and 2.6 ± 0.1 *D*, respectively, their real moments are more probably assigned the lower value of 2.2 ± 0.1 *D*. The presence of a moment in each case definitely excludes a *trans* coplanar configuration, a structure which had been anticipated as being highly probable. A *trans* planar configuration is possible for these two compounds only if rotation occurs about the C–O (alkyl) axis (Fig. 1a), there being no other method by which the moment could arise. In the free esters, to the contrary, evidence supports the view that no (restricted) rotation occurs[12] about the C–O axis containing the carbonyl carbon.

If a *trans* planar configuration is assumed for the chelates, their alkoxy groups would be in the same relative position (to each other) as those of hydroquinone dimethyl ether. The latter compound has a moment of 1.7 *D*[13] and is regarded as a "free-rotation" value. The moments of all the chelates are larger than this by amounts greater than any probable experimental error. The difference between these moments cannot be attributed to restricted rotation arising from steric interaction in hydroquinone dimethyl ether, since 4,4′-dimethoxydibenzene in which the alkoxy groups are further separated has nearly the same moment.[13] On this basis alone it was at first concluded that the larger moments of the chelates were only compatible with a tetrahedral configuration. In coming to this conclusion no allowance was made for any possible change in the C–O alkyl bond angle or in the O–alkyl bond moment. We are now of the opinion that it is not entirely valid to compare the moments of hydroquinone dimethyl ether and the ester chelates since those portions of the molecules separating the alkoxy groups are so different. A better comparison is probably made with the nickel xanthate complexes (Fig. 1b) which are diamagnetic and presumably planar.[8] The alkoxy groups in these compounds are in the same relative position as in the mercapto ester chelates and in addition a greater similarity exists between these molecules.

The dipole moments of bis-(isobutylxanthato)-nickel and bis-(isopropylxanthato)-nickel in benzene are 2.33 *D* at 22° and 2.60 *D* at 30°, respectively.[14] These values are in good agreement with those of the mercapto ester chelates.

The large increase in moment in passing from the nickel thioglycolate ester chelates to that of bis-(ethylthioacetoacetato)-nickel reflects a significant structural difference. If the molecule is planar, this increase can be attributed to: a change in the C–O–alkyl bond angle, a change in the O–alkyl bond moment and a change in the degree of freedom of rotation of the alkoxy groups about the C–O (alkyl) axis. These variations in turn can in part be attributed to that required upon passing from a five-membered saturated ring to a six-membered unsaturated ring and to resonance forms in the latter of the type



not possible in the former, which alters the double bond character of the C–O (alkyl) bond and therefore of rotation about this axis. If bis-(ethylthioacetoacetato)-nickel is tetrahedral, the only evidence supporting this being its ability to form a dipyridine compound, its moment would differ from the planar configuration but the actual value is difficult to predict.

The least probable structures for the compounds containing the thioglycolates, involving no chelation, would have moments of about 2.4–2.5 *D* corresponding to the dicarboxylic acid esters,[15] if one assumes a linear S–Ni–S grouping with all sulfur bonds coplanar and in the *trans* position. For complete freedom of rotation the moment was calculated to be 3.0 *D*, using the following equation and constants

$$\bar{\mu}^2 = 2m_1^2 + 2m_2^2 - 4m_1m_2 \cos\alpha \cos\beta \sin^2\gamma - 2m_1^2 \cos^2\alpha \cos^2\beta \cos^2\gamma - 2m_2^2 \cos^2\gamma$$

$m_1 = \mu\,(\mathrm{COOR}) = 1.9D$ $\beta = \sphericalangle\ \mathrm{SCC} = 110°$

$m_2 = \mu\,(\mathrm{C{-}S}) = 1.2D$ $\gamma = \sphericalangle\ \mathrm{NiSC} = 105°$

α = angle between resultant of ester group and carbon attached = 107°

Although both the open chain values are in good agreement with those observed, this structure is dismissed on the basis of chemical properties. The complexes can be shaken with strong alkali without effecting hydrolysis of the ester groups, which is contrary to what would occur if they were open to attack.

Acknowledgment.—Ethyl and hexadecyl thioglycolates were donated by Evans Chemetics, Inc. Methyl thiosalicylate was a gift of the Medical Chemicals Corporation. We wish to express our gratitude to Dr. N. Elliot of the Brookhaven National Laboratory for his assistance in the magnetic susceptibility measurements. This work was conducted under the auspices of the Atomic Energy Commission, contract number AT-(30-1)-906.

NEW YORK, N. Y.

---

[11] R. G. Charles and H. Freiser, THIS JOURNAL, **73**, 5223 (1951).

[12] J. M. O'Gorman, W. Shand, Jr., and V. Schomaker, *ibid.*, **72**, 4222 (1950).

[13] R. J. W. LeFevre, "Dipole Moments," Methuen & Co., London, 1948, p. 92.

[14] "Landolt-Börnstein," 6th Ed., Vol. 1, Part 3, Springer-Verlag, 1951, p. 489.

[15] C. P. Smyth and W. S. Walls, THIS JOURNAL, **53**, 528 (1931).