(30 ml.) added. The crude solid was fractionally crystallized from water by adding alcohol. The resolving agent then was removed from a concentrated aqueous solution of each fraction by the addition of potassium iodide. After removal of the iodide precipitate, the potassium salt of the chromium complex was caused to crystallize by the addition of alcohol. All fractions were inactive.

Infrared Spectra of Rhodium(III) and Chromium(III) Complexes.—The spectra of [$RhH_2O(H{\cdot}EDTA)$] and [$CrH_2O(H{\cdot}EDTA)$] were almost identical, showing peaks at 1742, 1643 and 1742, 1650 cm.$^{-1}$ in the carbonyl region. The peak at 1742 cm.$^{-1}$ has been assigned to the free carboxylic acid group, and the higher frequencies to the three coördinated carboxyl groups. The relative intensities of the peaks are in conformity with these assignments. No peak could be assigned unequivocally to the coördinated water molecule.

As expected, the spectra of $K[Rh(H_2{\cdot}EDTA)Cl_2]$ and $K[Rh(H_2{\cdot}EDTA)Br_2]$ were very similar. In the carbonyl region two peaks of comparable intensity and breadth were found, at 1720 cm.$^{-1}$ (two free carboxylic acid groups) and 1598 cm.$^{-1}$ (two coördinated carboxyl groups) for the former substance and at 1717 cm.$^{-1}$ and 1595 cm.$^{-1}$ for the latter.

Acknowledgments.—The authors are indebted to Mr. E. P. Serjeant and Dr. J. E. Fildes for assistance with the *pK* determinations and the microanalyses.

[Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin]

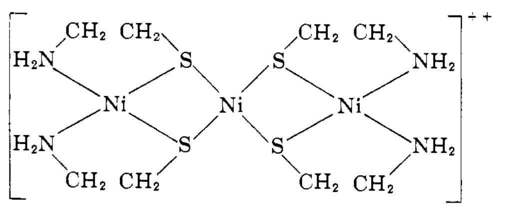
Polynuclear Complex Formation Between Nickel(II) and Mercaptoacetate Ions[1]

By D. L. Leussing, R. E. Laramy and Gene S. Alberts

Received February 24, 1960

Nickel(II) and mercaptoacetate ions react to form a series of polynuclear complexes of the composition $Ni[Ni(RS)_2]_n{}^{2-2n}$. The monomeric $Ni(RS)_2^{=}$ is also formed. The coexistence of both polynuclear and monomeric species in solution makes difficult an exact description of the system, but to a good approximation the solution equilibria can be described in terms of the species $Ni_4(RS)_6^{-4}$ and $Ni(RS)_2^{=}$. The stabilities of these species and also their heats and entropies of formation were determined from the temperature dependence of the formation function in the range 0 to 40°.

The formation of polynuclear complexes has been demonstrated in several systems with nickel(II) ions and mercaptide containing ligands. Jicha and Busch[2] have isolated tetrakis-(2-aminoethanethiol)-trinickel(II) dichloride. The nickel(II) ions in this complex were found to be diamagnetic[2] and therefore are in a tetragonal (square-planar) ligand field.[3] Jicha and Busch also found that analogous compounds could be prepared in which one of the nickel(II) ions is replaced by Co(II) or Cu(II). They propose the structure



where the central nickel ion is replaceable.

The ligand 2,3-dimercapto-1-propanol has been shown[4] to form a dimeric complex, $Ni_2(DMP)_3OH^{-4}$. Similarly, 1,2-ethanedithiol reacts[5] to form $Ni_2es_3^{=}$. Jensen[6] has attributed the high insolubility of bis-(*o*-aminothiophenolate)-nickel(II) to a network structure in which sulfur bridges join adjacent nickel ions.

In an earlier work with mercaptoacetate,[7] the formation function has been interpreted in terms of the mononuclear complexes $NiSCH_2CO_2$ and $Ni(SCH_2CO_2)_2^{=}$. This function describes $\bar{n}$, the average number of ligands complexed per metal ion in a system, as a function of the concentration of uncombined ligand. The present work represents a continuation of this earlier study. An attempt was made to determine the heats and entropies of the formation of the originally proposed complexes. To do this, the formation function was obtained at various temperatures. At the lower temperatures studied it was obvious that the simple explanation originally proposed did not fit the results. Polynuclear complexes appeared to be present in this system also. A detailed study was made to determine the nature of these complexes.

Experimental

The preparation of reagents and solutions and the procedures used were essentially the same as described earlier.[7] The formation function was calculated from the results of potentiometric titrations in which solutions of nickel nitrate (or chloride) and mercaptoacetic acid in 0.10 *M* potassium chloride were titrated with standard 1.0 *M* potassium hydroxide. During titration, the solutions were thermostated in a water-bath and were protected from air by vigorously bubbling a stream of nitrogen through them. The beakers which contained the solutions were capped by stoppers through which close fitting holes had been drilled for the electrodes, buret and bubbling tube.

Titrations were made at temperatures of 0, 15, 35 and 40°. In addition to being 0.10 *M* in KCl and 0.00206 *M* in nickel nitrate, the following solutions contained mercaptoacetic acid at concentrations of 0.00978 *M* at 0°, 0.01145 *M* at 35° and 0.00990 *M* at 40°. The effect of variation of the nickel concentration was studied at 15° also in 0.10 *M* potassium chloride. Solutions were titrated which contained 0.00255 *M* mercaptoacetic acid, 0.000489 *M* nickel chloride; 0.00259 *M* mercaptoacetic acid, 0.000978 *M* nickel chloride; 0.01020 *M* mercaptoacetic acid, 0.00254 *M* nickel chloride; and 0.01028 *M* mercaptoacetic acid, 0.00397 *M* nickel chloride. The ionic strengths in the regions of interest in these solutions varied from about 0.10 to 0.12 *M*.

The glass and saturated calomel electrode system was standardized at each temperature against a solution of 0.025 *M* disodium hydrogen phosphate, 0.025 *M* potassium dihydrogen phosphate made up with National Bureau

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[1] Financial assistance for this work was made available by grants from the National Science Foundation and the Wisconsin Alumni Research Foundation.

[2] D. C. Jicha and D. H. Busch, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] C. J. Ballhausen and A. D. Liehr, This Journal, **81**, 538 (1959).

[4] D. L. Leussing, *ibid.*, **81**, 4208 (1959).

[5] D. L. Leussing and G. S. Alberts, *ibid.*, **82**, 4458 (1960).

[6] K. A. Jensen, *Z. anorg. u. allgem. Chem.*, **252**, 227 (1944).

[7] D. L. Leussing, This Journal, **80**, 4180 (1958).

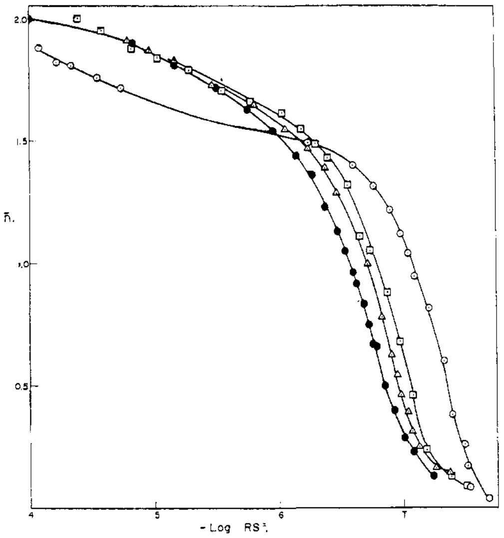

Fig. 1.—The formation of the nickel(II)-mercaptoacetate complexes: ○, 0°; □, 25°; △, 35°; ●, 40°. Concentrations are given in the text.

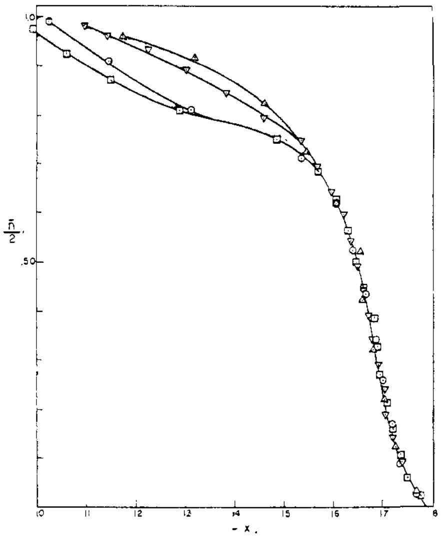

Fig. 2.—The formation of the nickel(II)-mercaptoacetate complexes at 15°: □, 0.00397 M Ni_{tot}; ○, 0.00254 M Ni_{tot}; ▽, 0.000978 M Ni_{tot}; △, 0.000489 M Ni_{tot}.

of Standards reagents and using the pH values assigned this buffer at each temperature.

The proton dissociation constants, K_{1a} and K_{2a}, for mercaptoacetic acid were determined at each temperature by the potentiometric titration of an approximately 0.010 M solution of the acid in 0.10 M potassium chloride with 1.0 M potassium hydroxide. The results are given in Table I. The values determined in the earlier study[7] at 25° also are given.[8]

As in ref. 7, we shall let the symbol $RS^=$ represent the mercaptoacetate ion. Quantities in parentheses shall refer to the actual concentration of the species enclosed, the subscript "tot" shall refer to the total analytical concentration of the substance so designated.

Values of $\bar{n}$ and $-\log (RS^=)$ were calculated from the titration curves in the presence of metal ions using the customary procedures.[9]

Absorption spectra were determined with the air-free cells previously described.[4] A thermostated cell block maintained the cells at the desired temperature.

Results

The results for 0, 25, 35 and 40° are presented in Fig. 1 as a plot of $\bar{n}$ *versus* $-\log (RS^=)$. The results for 15° are presented in slightly different form in Fig. 2, in which a plot is given of $\bar{n}/2$ *versus* the quantity x which is equal to the sum $\log (Ni)_{tot} + 2 \log (RS^=)$.

The curves for 0° in Fig. 1 and for 15° at the higher nickel concentrations in Fig. 2 show plateaus in the region $\bar{n}$ equals 1.5 to 1.6. A plateau in the formation curve indicates that a complex is formed which is appreciably stable relative to higher complexes. The non-integral value of $\bar{n}$ suggests that a polynuclear complex is formed. A polynuclear complex also is indicated by the data of Fig. 2 which show that $\bar{n}$ is not a function of $(RS^=)$ alone but in addition also depends upon $(Ni)_{tot}$.

Treatment of the data at 15° according to the method of Sillén[10a,b] shows that a "core plus links" series of complexes is formed, as a plot of $(Ni)_{tot}$ *versus* $-\log (RS^=)$ at a given $\bar{n}$ below 1.3 gives a straight line of slope two. Such behavior is implied in Fig. 2 where it is seen that all the points below $\bar{n}/2$ equals 0.7 fall on the same curve. These results indicate that the general composition of the complexes is $Ni[Ni(RS)_2]^{(2-2n)}$.

Above $\bar{n}/2$ equal to 0.70, the points deviate from the polynuclear curve in the order of decreasing $(Ni)_{tot}$. This deviation occurs because of the conversion of the polynuclear complexes to the monomeric $Ni(RS)_2^=$. In this region, $\bar{n}$ is a much more complicated function of $(Ni)_{tot}$ and $(RS^=)$ than is the case for either purely "core plus links" complexes or purely monomeric complexes.

The individual formation constants for the complexes $Ni_2(RS)_2$, $Ni_3(RS)_4^=$, $Ni_4(RS)_6^{==}$,.., are given by the general equation

$$q_n = \frac{(Ni_{n+1}(RS)_{2n}{}^{(2-2n)})}{(Ni^{++})u^n}$$

where, after Sillén,[10] u is equal to the product $(Ni^{++})(RS^=)^2$.

The formation constant for $Ni(RS)_2^=$ is given by

$$Q_2 = \frac{(Ni(RS)_2^=)}{u}$$

From the mass balance and the definition of $\bar{n}$,[9] it can be shown that

$$(Ni)_{tot} = (Ni^{++})(1 + 2q_1u + 3q_2u^2 + 4q_3u^3 + \ldots) + Q_2u \quad (1)$$

$$\frac{\bar{n}}{2} = \frac{(Ni^{++})(q_1u + 2q_2u^2 + 3q_3u^3 + \ldots) + Q_2u}{(Ni^{++})(1 + 2q_1u + 3q_2u^2 + 4q_3u^3 + \ldots) + Q_2u} \quad (2)$$

Sillén[10b] gives curve fitting methods for obtaining solutions for the constants in equations of this type

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[8] The value of K_{1a} at 25° in Table I appears to be high by an amount equivalent to about 0.08 pK_a units, since the 15° value has been duplicated by two different workers. The values of the formation function at 25° were taken from the earlier data, and it was felt best to use the acid dissociation constants determined at the same time as these rather than to use new constants. Besides the values are not sensitive to K_{1a} since complex formation does not take place until the first proton of mercaptoacetic acid is almost completely neutralized. The K_{2a} values, on the other hand, appear to be consistent.

[9] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[10] (a) L. G. Sillén, *Acta Chem. Scand.*, **8**, 299 (1954); (b) *ibid.*, **8**, 318 (1954).

where the terms in Q_2 are absent. In these methods the equations are reduced to two parameters by assuming some relationship between the q_n. Such a relationship is chosen so that a simple generating function can be substituted for the infinite series describing the polynuclear complexes in the mass equations. Generalized families of curves have been prepared for various relationships between the q_n and are illustrated in reference 10b.

Qualitatively by comparing Figs. 1 and 2 of the present work with Figs. 2a-c of reference 10b it can be seen that the functions chosen by Sillén do not describe the data for nickel(II) mercaptoacetate. In particular, the Sillén functions do not give a plateau as observed here.

We have assumed a relation between the q_n so that a hyperbolic cosine function can be substituted for the series of q_n in equations 1 and 2. Such a function was chosen because the series defining the hyperbolic cosine converges more rapidly than do the series for those functions chosen by Sillén. Also, tables of its values are readily available.

The cosh function can be substituted for the infinite series in equations 1 and 2 by assuming that $q_1 = q_0q/2!$, $q_2 = q_0(q)^2/4!$, $q_3 = q_0(q)^3/6!$, etc. To obtain a fit of the curves which are calculated from the resulting equations, it was found further necessary to consider negligible the concentration of $\mathrm{Ni_2(RS)_2}$. With these modifications and after making the substitution $v = qu$, it can be shown that equations 1 and 2 become

$$(\mathrm{Ni})_{\mathrm{tot}} = (\mathrm{Ni}^{++})\left[1 + \frac{q_0}{2}(2\cosh v^{1/2} + v^{1/2}\sinh v^{1/2} - 2v - 2)\right] + \frac{Q_2 v}{q} \quad (3)$$

$$\frac{\bar{n}}{2} = \frac{(\mathrm{Ni}^{++})\dfrac{q_0}{2}(v^{1/2}\sinh v^{1/2} - v) + Q_2\dfrac{v}{q}}{(\mathrm{Ni}^{++})\left[1 + \dfrac{q_0}{2}(2\cosh v^{1/2} + v^{1/2}\sinh v^{1/2} - 2v - 2)\right] + Q_2\dfrac{v}{q}} \quad (4)$$

The terms in Q_2 are negligible when the concentration of $\mathrm{Ni(RS)_2^{=}}$ is negligible and $\bar{n}/2$ becomes a function only of the variable v and the parameter q_0.

A family of curves for various values of q_0 was constructed of $\bar{n}/2$ *versus* the quantity X, where X is also a function of only q_0 and v and is given by

$$X = x + \log q = \log v + \log\left[1 + \frac{q_0}{2}(2\cosh v^{1/2} + v^{1/2}\sinh v^{1/2} - 2v - 2)\right]$$

These calculated curves then were superimposed over that observed in Fig. 2. A fit was obtained with the curve calculated using a value of q_0 equal to 0.060. The value of q was found to be 1.3×10^{13}. This was obtained from the relationship $\log q = X - x$ for matching points on the observed and calculated curves. In fitting the curves, the curve observed for the highest nickel concentration was used in the region $\bar{n}/2$ equals 0.7 to 0.8.

Using these results for q_0 and q, values of Q_2 were calculated to be $6 \times 10^{+12}$ from the point $\bar{n}$ equals 1.78 at 0.00397 M $(\mathrm{Ni})_{\mathrm{tot}}$ and $4 \times 10^{+12}$ from the point $\bar{n}$ equals 1.88 at 0.000489 M $(\mathrm{Ni})_{\mathrm{tot}}$.

The relation between the constants which is assumed in order to make the cosh substitution is artificial, and it is to be expected that only by accident would the values of the individual q_n resemble the true values. However, the qualitative facts which emerge in fitting such a function to the data are extremely valuable: first, the primary member of the series $\mathrm{Ni_2(RS)_2}$ is not important as far as the mass relationships are concerned; secondly, the q_n fall off rapidly with increasing values of n; thirdly, the value of Q_2 which is obtained is large enough to indicate that even in the most concentrated nickel solution investigated, low but appreciable concentrations of $\mathrm{Ni(RS)_2^{=}}$ are present.[11]

The omission of the Q_2 terms in equations 3 and 4 results in an approximation which is fairly good up to $\bar{n}$ values slightly greater than one for the most concentrated nickel solution investigated. At higher $\bar{n}$ values the approximation breaks down. Therefore interference by $\mathrm{Ni(RS)_2^{=}}$ prevents obtaining a quantitative description of the stabilities of the higher complexes with the present data. However, the error introduced by neglecting $\mathrm{Ni(RS)_2^{=}}$ in the above treatment is such as to attribute too large values to the constants for the higher polynuclear complexes. The values of $\bar{n}$ in the region of the plateau indicate that $\mathrm{Ni_4(RS)_6^{-4}}$ is appreciably stable but the stabilities of the polynuclear complexes higher than this must drop off even faster than is indicated by the above values of q_0 and q with the rapidly converging cosh function.

Therefore, since terms for only two polynuclear complexes appear to be significant in equations 1 and 2, the direct analysis proposed by Sillén[10] was tried using the data where the previous results indicate that $\mathrm{Ni(RS)_2^{=}}$ is negligible (no more than 2–3% of $(\mathrm{Ni})_{\mathrm{tot}}$). In this method the areas under the curve of a plot such as Fig. 2 are determined for chosen points, and these are used to obtain simultaneous equations linear in the q_n. The result of this treatment is that at 15° the contribution of $\mathrm{Ni_3(RS)_4^{=}}$ is small, being about the same order as the experimental error, and at 0° its contribution is entirely negligible. Values of q_3, the constant for $\mathrm{Ni_4(RS)_6^{=}}$, are calculated to be $3.5 \times 10^{+50}$ at 15° and $69 \times 10^{+50}$ at 0°.

It is seen from these results that the complexes $\mathrm{Ni_4(RS)_6^{-4}}$ and $\mathrm{Ni(RS)_2^{=}}$ are predominant and to a good approximation only the constants q_3 and Q_2 need be considered in describing the system. Because of the great simplification it is very easy to solve for q_3 and Q_2 using the simultaneous equations expressing the $(\mathrm{Ni})_{\mathrm{tot}}$ and $(\mathrm{RS})_{\mathrm{tot}}$ mass balance at two experimental points. An iteration procedure is used most easily. Results calculated in this manner are given in Table I.

The values of q_3 at 0 and 15° in Table I are in very good agreement with those values calculated

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(11) A value of $\bar{n}/2$ equal to 0.18 in Fig. 2 corresponds to v equals 6.00 and a concentration of $\mathrm{Ni(RS)_2^{=}}$ about 3×10^{-5} M. This is only 0.8% of the nickel at 0.00397 M $(\mathrm{Ni})_{\mathrm{tot}}$ but is 6% at 0.000489 M $(\mathrm{Ni})_{\mathrm{tot}}$. At $\bar{n}/2$ equals 0.54, the value of v is 14.8 and the concentration of $\mathrm{Ni(RS)_2^{=}}$ is proportionately greater.

TABLE I

THE FORMATION CONSTANTS FOR THE NICKEL(II) MERCAPTOACETATE COMPLEXES IN 0.10 *M* POTASSIUM CHLORIDE

T, °C.	K_{1a},[a] × 10^{+4}	K_{2a},[a] × 10^{+11}	q_2, × 10^{-33}	q_3, × 10^{-50}	Q_2, × 10^{-12}
0	3.8	3.3	...	67	14
15	2.8	4.5	...	4.7	11
25[b]	3.3	7.6	...	0.7	11
35	2.6	8.5	(3)	.17	8
40	2.2	11.2	(0.5)	.03	5

[a] The proton dissociation constants of mercaptoacetic acid. [b] From the data of ref. 7.

above using Sillén's direct method. Theoretical points were calculated using the values in Table I and as a check were compared with those observed. Only for the curves at 35 and 40° at $\bar{n}$ values less than 0.2 were differences greater than 0.05 $\bar{n}$ unit obtained between the observed and calculated points. The difference is such as to be caused by the presence of $Ni_3(RS)_4^{=}$ which is favored in this region. An estimate of q_2 was obtained by solving for this term in equations 1 and 2 using the values of q_3 and Q_2 already given and the experimental data for a point in the region $0.2 > \bar{n} > 0.1$. These results also are given in Table I. Because of the high percentage error in $\bar{n}$ for small values, the result for q_2 is not highly accurate but the order of magnitude is obtained.

The temperature dependence of Q_2 leads to values of ΔH_{298} equal to -3.5 ± 1 kcal. mole^{-1} and ΔS_{298} equal to 48 cal. mole^{-1} deg.$^{-1}$ for the reaction $Ni_{aq}^{++} + 2RS_{aq}^{=} \rightarrow Ni(RS)_{2aq}^{=}$. The temperature dependence of q_3 gives values of ΔH_{298} equal to -31 ± 2 kcal. mole^{-1} and ΔS_{298} equal to $+124$ cal. mole^{-1} deg.$^{-1}$ for the reaction $4Ni_{aq}^{++}\ 6RS_{aq}^{=} \rightarrow Ni_4(RS)_{6aq}^{-4}$. An interesting feature of this is that the heat of formation of $^1/_4\, Ni_4(RS)_6^{-4}$ is about twice that of $Ni(RS)_2^{=}$.

The positive entropies of reaction are of the same order as is usually observed for reactions between oppositely charged ions,[12] in contrast to the negative entropies observed between metal ions and neutral ligands.[13,14]

In Fig. 3 a plot of the absorbances of nickel(II) mercaptoacetate solutions at 512 and 438 mu is given as a function of $\bar{n}$. The absorbance at each wave length increases with increasing $\bar{n}$ until a maximum is reached. Then a decrease occurs due to the conversion of the intensely colored polynuclear complexes to the less highly colored $Ni(RS)_2^{=}$. The value of $\bar{n}$ at the maximum should be 1.50 if only $Ni_4(RS)_6^{==}$ were formed. Instead, the maximum is seen to lie at higher $\bar{n}$ values showing the formation of spectroscopically significant amounts of higher polynuclear complexes. This evidence of their formation lends additional support to the "core plus links" series which is proposed.

As the temperature of a solution at a given $\bar{n}$ decreases the absorbance increases. From the behavior of the formation constants with temperature, this effect can be attributed to a shift in equilibrium which favors the polynuclear complexes with decreasing temperature. The extinction coefficients of $Ni_4(RS)_6^{==}$ which are calculated from spectra resolved using the formation constants in Table I, are found to be the same at 0 and 25°. The extinction coefficients of $Ni(RS)_2^{=}$ are also the same at these two temperatures.

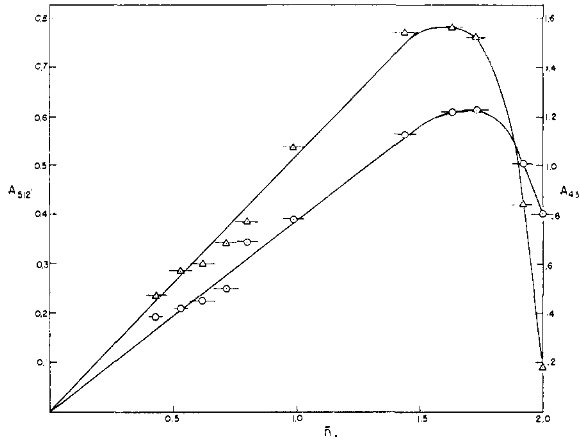
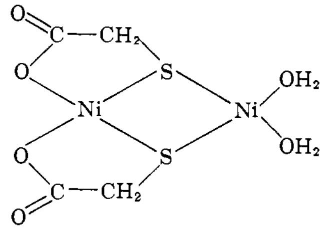


Fig. 3.—The absorbance of nickel (II.)-mercaptoacetate solutions as a function of the degree of complex formation, 0.00206 *M* $Ni(NO_3)_2$, 25°, 2.00 cm. cells: Δ, 438 mμ; O, 512 mμ.

Discussion

The absorption spectrum of $Ni_4(RS)_6^{==}$ which has been given[7] as that of NiRS is strikingly similar to those of $Ni_2(DMP)_3OH^{-4}$ and $Ni_2es_3^{=}$.[5] The broad bands which arise in the near infrared and attain extinction coefficients of about 10^{+4} in the near ultraviolet seem to be characteristic of the polynuclear complexes and give evidence for a similar structure in these unusual and interesting species.

The structures of the polynuclear nickel(II)—mercaptoacetate complexes can be described easily using as a basis the multiply coördinated sulfur structure already proposed for the tetrakis-(2-aminoethanethiol)-trinickel(II) ion.[2] The first member in the series, $Ni_2(RS)_2$, can be visualized as having the structure



Here the low stability can be attributed to the water molecules that are coördinated to the (presumably) square-planar nickel(II) ion. No complex with water molecules occupying the square-planar position of diamagnetic nickel(II) appears to have been reported. Apparently such complexes are unstable and the water molecules are easily replaced by more polarizable ligands. This can take place to give the next member of the series with the structure

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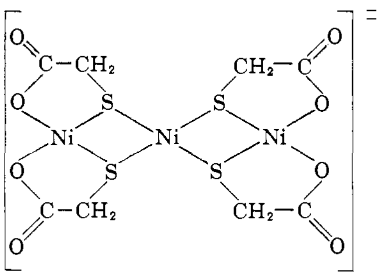
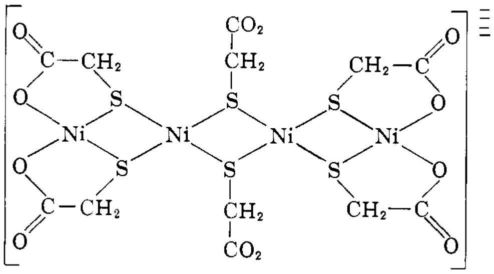
(12) See, for example, E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

(13) I. Paulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955).

(14) D. L. Leussing, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.



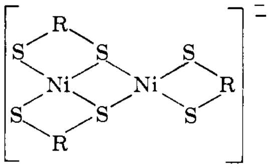
The third member can be formed from the second by the displacement of two adjacent carboxylate groups to give



This is plausible because of the relatively weak complexing of the carboxylate group with the divalent transition metals compared to that of the mercaptide group (see refs. 4 and 7). The carboxylate groups which are coördinated to nickel must certainly be hydrated in aqueous solution. This may be the source of the extra heat (and stability) noted above for $Ni_4(RS)_6^{-4}$.[15]

Higher complexes can be built up by a repetition of the last process. But then uncoördinated carboxylate groups appear adjacent to each other in the polymer and charge repulsion must bring about a decrease in stability.

On this basis it is also possible to explain the fact that with the dithiols only dimeric complexes are observed. The structure of these can be pictured as



where all the square-planar positions on the nickel(II) ions are occupied by sulfur atoms, and therefore a further increase in chain length is not feasible.

The sulfur atoms in the polymeric complexes would tend to develop a positive charge because of the multiple bonding to the nickel ions. This positive charge may be relieved by the back donation of electrons from the metal ions to the sulfur through π bonding.[16] In this may lie the reason for the pronounced spectral differences between the polymeric and monomeric complexes. The bonding appears to be predominantly σ in these latter.[4]

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(15) Referee I points out that there are 3(Ni–S) and 1(Ni–O) bonds per nickel in the tetramer but 2(Ni–S) and 2(Ni–O) bonds in the monomer and that higher bond energy of Ni–S relative to Ni–O would account for the observation. However, a comparison of the Ni–S bonding between the tetramer and monomer is obscured by the fact that in the tetramer the sulfur is multiply bonded to metal ions, whereas, in the monomer it is only singly bonded. A clear-cut distinction between the relative importance of the NiS bonding and the hydration of the carboxylate groups toward the heat of formation of the tetramer therefore cannot be made. Both factors should be considered then. We wish to thank Referee I for suggesting this additional possibility.

(16) A similar MS_2M ring system has been reported to be formed with either Pd(II) or Pt(II). The S-Pt-S-Pt ring is claimed to be "aromatic" in character (J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953)).

[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

The Complexes of Nickel(II), Palladium(II) and Platinum(II) with 2-Pyridinaldoxime[1]

BY RONALD A. KRAUSE AND DARYLE H. BUSCH

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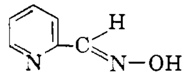
Several complexes of nickel(II), palladium(II) and platinum(II) with 2-pyridinaldoxime (HPOX) have been prepared, characterized, and compared with the complexes formed by the similar ligands dimethylglyoxime, 2,2′-bipyridine and 2-methyl-2-amino-3-butanone oxime. Nickel(II) has been observed to form a number of complexes, the most typical of which are $[Ni(HPOX)_3]I_2$, $[Ni(HPOX)_2Cl_2]$, [Ni(HPOX)(POX)]I and $[Ni(POX)_2]$. All of the nickel(II) complexes are paramagnetic, with magnetic moments which indicate the presence of two unpaired electrons. The magnetic moment of the uncharged nickel(II) complex $[Ni(POX)_2]$ is associated with an unusually high Weiss constant. Palladium(II) forms the typical square planar complexes [Pd(HPOX)(POX)]Cl and $[Pd(POX)_2]$, while platinum(II) forms $[Pt(POX)_2]$.

Introduction

No detailed study has yet been reported on the nickel(II), palladium(II) and platinum(II) complexes of an aromatic amine-oxime. Tschugaeff[2] first prepared palladium(II) and platinum(II) complexes of phenyl-α-pyridyl ketoxime, and Emmert and Diehl[3] later reported on the reaction of methyl-α-pyridyl ketoxime with nickel(II). Both studies, however, were of a cursory nature. The present investigation is concerned with the nickel(II), palladium(II) and platinum(II) complexes of a similar aromatic amine-oxime, 2-pyridinaldoxime (HPOX) (I).



I

It can be seen readily that HPOX shows structural features of two well known ligands, 2,2′-

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(1) Abstracted from the Ph.D. dissertation of R. A. Krause, The Ohio State University, 1959. Portions of this work were presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., 1959.

(2) L. Tschugaeff, *Chem. Ber.*, **39**, 3382 (1906).

(3) B. Emmert and K. Diehl, *ibid.*, **62B**, 1738 (1929).