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A Polarographic Study of Metal Dithio-β-diketonates[*1]

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The synthesis and the infrared or visible spectroscopic properties of metal dithio-β-diketonates have been potentially sutided very recently.1-6) Concerning the abnormal valency states of the central metal ion of the five-membered-ring dithiolate chelates, nickel dithiolate complexes have been extensively studied polarographically,7-8) and it has been shown that the half-wave potentials of the dithiolates correlate linearly with Taft's substituent constants.8) However, the polarographic behavior of the six-membered-ring dithio-β-diketonates has not yet been reported on. In our last paper4) we reported that the dithioacetylacetonate was more stable than the other dithio-β-diketonates, which contain a phenyl or trifluoromethyl group rather than the one or two methyl groups of the former. The correlation between the polarographic and spectroscopic behavior of these chelates will be discussed in this paper.

Experimental

Reagents. All the metal chelates were synthesized by a method reported in previous papers.3-4) The lithium chloride and the sodium perchlorate were of a guaranteed reagent grade and were used without further purification. The organic solvents were purified by a standard technique.9)

Apparatuses and Experimental Procedure. A model PA-101 pen-recording d. c. polarograph of the Yanagimoto Mfg. Co., Ltd., and a dropping mercury electrode were employed. The reference electrode was a saturated calomel electrode (SCE); it was connected to the cell by means of a salt bridge (aqueous potassium chloride-agar gel). The liquid junction potential was not measured in this experiment.

Results and Discussion

In a dimethylformamide (DMF) solution, these chelates show three waves. The polarogram of nickel dithioacetylacetonate is shown in Fig. 1. The diffusion-controlled current, i_d, of the sum of the first and the second waves was proportional to the concentration of the chelate in the region of $2\times10^{-4}-2\times10^{-3}$M, and the $i_d/\sqrt{h_{eff}}$ ratio (h_{eff}: the mercury head corrected for the back pressure) of the first wave was almost constant. A plot of log $i/(i_d-i)$ *versus* the potential, E, of the first wave is shown in Fig. 2. The linear portion of

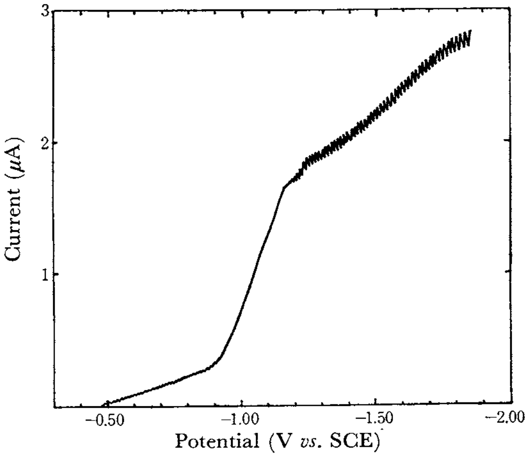

Fig. 1. D.c. polarogram of dithioacetylacetonatonickel(II).
Solvent = dimethylformamide
Concentration of the chelate = 2 mM
Concentration of the lithium chloride = 1 M

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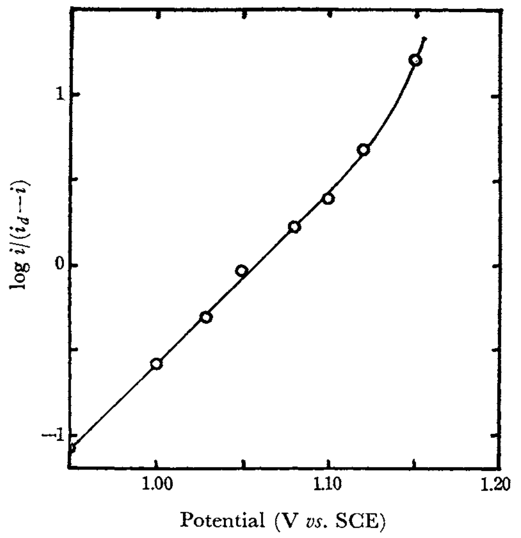

Fig. 2. The d.c. log-plot analysis for bis(dithioacetylacetonato)nickel(II).
Solvent=DMF
Concentration of the chelate=2 mM
Concentration of lithium chloride=1 M

the plot gave a slope of approximately 100 mV. From these results it seems that the wave is somewhat irreversible. The other dithio-β-diketonates give similar polarograms, though they seem to be more irreversible.

The color of the solution of trifluoromethyl derivatives changes from green to red several minutes after dissolution, perhaps because of the fast solvolysis reaction of the chelate. The polarogram of the species was obtained by using the red solution 1 to 5 hr after dissolution. The half-wave potentials of the dithio-β-diketonates and related compounds in various solvents are summarized in Table 1.

The acetonitrile solutions of nickel dithio-β-diketonates show a wave of $E_{1/2}=-1.0$—-1.1 V *vs.* SCE. On the other hand, those of nickel(II) chloride show a wave of $E_{1/2}=1.05$ or 1.03 V in a 1 M $NaClO_4$ and a 1 M LiCl aqueous solution respectively, while nickel(II) acetate shows a wave of $E_{1/2}=1.06$ V in 1 M $NaClO_4$. Accordingly, the waves of $E_{1/2}$ = *ca.* −1.0 V *vs.* SCE are probably due to Ni(II)→Ni(0).

In DMF solutions, the first of the three waves seems to be that of the reduction of chelated nickel: Ni(II)→Ni(0). The second wave is lower than the first one and it overlaps with the first one a little. The third wave is unclear because of the superposed wave of the electrolyte; it is probably the reduction wave of the organic part of the ligand.

Since the half-wave potential of the wave of nickel chloride in DMF is close to that of the second wave, the second wave may correspond to the reduction of the nickel chelate, partly solvolysed by the DMF in the solution. In fact, the chelates such as trifluoromethyl derivatives, which are solvolyzed easily by DMF, give larger wave heights. The sum of the heights of the first and the second waves is always approximately the same at any given concentration of the dissolved metal chelate,

TABLE 1. THE HALF-WAVE POTENTIALS OF THE CHELATES AND RELATED COMPOUNDS

Supporting electrolyte	0.5 M $NaClO_4$	1 M $NaClO_4$				0.2 M LiCl			
Solvent	Acetonitrile	Dimethylformamide				Dimethylformamide			
Waves		1st	2nd	3rd	2nd/1st*	1st	2nd	3rd	2nd/1st*
Compound									
$NiCl_2$	1.03		1.20				1.40		
$Ni(sacsac)_2$	1.12	1.09	1.25	1.58	0.29	1.06	1.22	1.66	0.15
$Ni(sbzsac)_2$	1.08	0.96	1.18	1.64	0.75	0.96	1.26	1.77**	0.60
$Ni(sbzsbz)_2$	1.08	0.86	1.12	1.52	0.48	0.80	1.36	1.52**	0.31
$Ni(sfasac)_2$	(0.60) 0.97 (1.27)	0.90	1.04	1.66	3.2	1.01	1.30	1.70	3.5
$Ni(sfasbz)_2$	(0.67) 0.94 (1.50)	0.72	1.09	1.64	1.6	0.78	1.24	1.47**	1.5
$Ni(L_{ss}L_{so})_2$						0.95	1.12	1.71	0.48
$Ni(L_{so})_2$						0.97	1.12	1.70	1.10
$CoCl_2$	1.06		1.34	1.63			>2.00		
$Co(sacsac)_2$	1.06	0.94	1.28		0.20	0.93	1.34		0.36

$Ni(sacsac)_2$: Bis(dithioacetylacetonato)nickel(II)
$Ni(sbzsac)_2$: Bis(dithiobenzoylacetonato)nickel(II)
$Ni(sbzsbz)_2$: Bis(dithiodibenzoylmethanato)nickel(II)
$Ni(sfasac)_2$: Bis(dithiotrifluoroacetylacetonato)nickel(II)
$Ni(sfasbz)_2$: Bis(dithiotrifluorobenzoylacetonato)nickel(II)
$Ni(L_{ss}L_{so})$: Dithioacetylacetonatomonothioacetylacetonatonickel(II)
$Ni(L_{so})_2$: Bis(monothioacetylacetonato)nickel(II)
* The ratio of 2nd and 1st wave heights. (5×10^{-4} M NiL_2; 1 to 3 hr after dissolution)
** Not well-defined owing to the overlapping of the waves.

even if the ligands of the chelates are not the same. This fact also seems to show that both the first and second waves are Ni(II)→Ni(0) reduction waves.

The ratio between the heights of the first and the second waves seems to be related to the ratio between the chelated and solvolyzed species in the solution. However, the evaluation of the stability constants attempted in the present work was not successful because of various unknown factors.

Dithioacetylacetonatomonothioacetylacetonatonickel(II) and bis(monothioacetylacetonato)nickel(II) show a small maximum wave between the first and the second wave. The ratio of the second wave height to the first one increases depending on the number of oxygen atoms introduced into the ligands, though the half-wave potentials of both waves do not show any appreciable change.

It is very interesting that the half-wave potential of the first wave of nickel chelates is more positive than that of simple nickel salt in a DMF solution. Perhaps because of the special coordinate bond character between sulfur and the central metal, as well as because of the pseudo-aromaticity of the dithio-β-diketonate chelate ring, electrons are more easily supplied to the central ion than usual complexes; this should cause a positive shift of the wave. On the other hand, the more stable a complex is, the more the wave shifts toward negative potentials. In this case, the former effect is predominant, and the first wave shows a positive shift. The first wave of bis(dithioacetylacetonato)cobalt(II) also shows the same tendency.

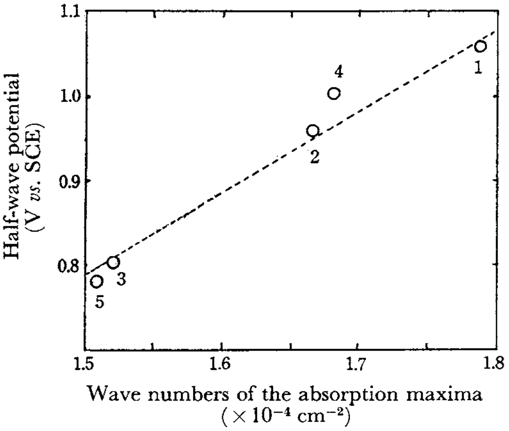

Fig. 3. Relation between the half-wave potential of the first wave and the wave numbers of the absorption maxima.
1. Ni(sacsac)$_2$ 2. Ni(sbzsac)$_2$ 3. Ni(sbzsbz)$_2$ 4. Ni(sfasac)$_2$ 5. Ni(sfasbz)$_2$

The relation between the wave number of the maxima of the electronic spectral band in the 500-to-600 mμ region of the chelates and the half-wave potentials of their first waves is shown in Fig. 3. According to Schrauzer *et al.*,[8] the half-wave potential of the polarograms of five-membered-ring dithiolate chelates shifts toward more positive potentials when Taft's inductive coefficients of ligands are higher. Although this phenomenon is also to be expected for the dithio-β-diketonates, the Taft constants for the six-membered-ring chelates containing a trifluoromethyl group, as calculated by the method of Schrauzer *et al.*,[8] are too high and are not in any linear relation with the $E_{1/2}$ and $\sum\sigma^*$.

In the case of five-membered-ring dithiolate complexes, the waves near -1.0 V and $+0.1$ V *vs.* Ag/AgCl were assigned to Ni(I)→Ni(0) and Ni(II)→Ni(I) respectively. However, the six-membered-ring dithio-β-diketonato chelates do not give the latter wave; moreover, it is not probable to identify any of the waves as an Ni(I)→Ni(0) one; consequently, it can be said that dianionic or monoanionic species are not stable in the case of six-membered-ring chelates. This is probably because of the weaker aromaticity of the latter chelate ring.

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