scheme coefficient was \( p = 0.08 \), the \( f \)-curves used and corrections for anomalous dispersion, \( \Delta f \) and \( \Delta f' \), are given, e.g., in ref. 6. All the calculations were performed with the help of a PDP11/23 mini-computer using the SDP-PLUS program package of the Enraf-Nonius company.

References


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Complexes of \( \text{Ni}^{2+} \) with dioxotetramines and macrocyclic tetraaza-ligands as inhibitors of oxidation of dialkyl sulfoxides

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Nickel complexes with acyclic dioxotetramines and macrocyclic tetraaza-ligands, when present in dimethyl sulfoxide, inhibit its radical chain oxidation with oxygen, as shown by the volumetric method. A scheme of the processes involving the decay of \( \alpha \)-sulfinylperoxyl radicals upon interaction with both \( \text{Ni}^{2+} \) and \( \text{Ni}^{3+} \) ions is proposed.

Key words: nickel, complexes; tetraaza macrocycles; dioxotetramines; oxidation inhibitors; dialkyl sulfoxides.

Dialkyl sulfoxides (\( \text{R}_2\text{SO} \)) are compounds of extensive practical use.1,2 However, due to their low thermal stability, on storage and application they undergo autooxidative transformations which deteriorate their physical, chemical, and technical properties (see refs. 3 and 4).

It has been shown previously5 that the oxidation of \( \text{R}_2\text{SO} \) with oxygen proceeds by the radical chain mechanism, the chain transfer being accomplished by \( \alpha \)-sulfinylalkyl (\( \text{RS(O)(C)} \cdot \text{C} < \)) and \( \alpha \)-sulfinylperoxyl (\( \text{RS(O)(C)} \cdot \text{OO} \cdot \)) radicals. Coordination compounds of transition metals have been shown6 to be potential inhibitors of this process, since they can react repeatedly with \( \alpha \)-sulfinylperoxyl radicals

\[
\text{RS(O)(C)} \cdot \text{OO} \cdot ^+ + \text{M}^{n+} \rightarrow \text{RS(O)(C)} \cdot \text{OO} \cdot ^+ + \text{M}^{(n+1)+}, \tag{1}
\]

\[
\text{RS(O)(C)} \cdot \text{OO} \cdot ^+ + \text{M}^{(n+1)+} \rightarrow \text{RS(O)(C)} \cdot \text{O} ^+ + \text{O}_2 + \text{M}^{n+}, \tag{2}
\]

where \( \text{M}^{n+} \) and \( \text{M}^{(n+1)} \) represent the central atom of the complex in two different oxidation states. In continuation of a search for coordination compounds capable of chain termination in the oxidation of \( \text{R}_2\text{SO} \) we have studied complexes of nickel with tetraaza macrocyclic ligands (\( \text{L}^1\text{L}^2\text{L}^3 \)) and with dioxotetramines (\( \text{H}_2\text{L}^5, \text{H}_2\text{L}^7 \)) (Scheme 1, compounds 1-5, 8 and 6, 7, respectively).
Complexes of Ni$^{2+}$ with tetraaza-ligands

**Scheme 1**

![Chemical structures](image)

We have chosen these compounds since the above-mentioned ligands not only form very stable complexes with Ni$^{2+}$ ions but also provide both kinetic and thermodynamic stabilization of the higher oxidation state of nickel (+3). Besides, such compounds have been shown to be effective oxidation inhibitors for rubbers.

**Experimental**

All the reagents were of the "pure for analysis" or "chemically pure" grade and were used without additional purification. Dimethyl sulfoxide (DMSO) was purified by a standard procedure. Complexes of Ni$^{2+}$ with the ligands L$_1$--L$_5$ and H$_2$L$_6$, H$_2$L$_7$ were prepared and purified according to ref. 10. A Ni$^{2+}$ complex [NiL$_4$(SO$_4$)$_2$H$_2$O]ClO$_4$ (8) was prepared by the procedure given in ref. 11.

The electron absorption spectra were run on a Specord UV-Vis instrument. The ESR spectra of the frozen DMSO solutions were recorded with a Varian E9 spectrometer. Cyclic voltammograms were measured with a three-electrode circuit using a Pt 50--1.1 potentiostat connected with a PR-8 programmer and an XY Recorder A3 (a two-coordinate self-recorder). A platinum point electrode was used as the working electrode, a platinum wire served as the auxiliary electrode, and a saturated calomel electrode was applied as the reference. Potential measurements in dimethyl sulfoxide solutions were referred to the ferrocenium(+)/ferrocene redox-pair as an internal standard. NaClO$_4$ (0.1 M) was used as the background electrolyte. The rate of the potential sweep was 50 mV s$^{-1}$.

The inhibiting properties of the Ni$^{2+}$ complexes were studied under initiated oxidation of dimethyl sulfoxide (100 °C) using a volumetric unit. Radical chain oxidation was initiated by azobiscyclohexanitrile.

**Results and Discussion**

The investigations have shown that the coordination compounds of Ni$^{2+}$ efficiently decelerate the oxidation of DMSO, whereas Ni(ClO$_4$)$_2$ does not possess inhibiting properties (Fig. 1). Compounds 1 and 4 display ambivalent properties (Fig. 2): when the initial concentration of the complex is low, the oxidation process is accelerated (due to the free-radical decomposition of hydroperoxides, see ref. 12). An increase in the concentration of the complex decelerates the oxidation. The dependences observed for compounds 1 and 8 are similar. Since these complexes contain the metal ion in different oxidation states, one can infer that the general course of the process does not depend on the initial oxidation state of the central ion (Ni$^{2+}$ or Ni$^{3+}$), at least, for the complexes with the ligand L$_1$.

For all the compounds studied the oxidation rate ($w$) reaches a limiting value, and at sufficiently high concentrations does not depend on the content of the complex in the solution (Figs. 2, 3). Free polyamine ligands do not affect the rate of DMSO oxidation (Fig. 3), or their inhibiting efficiency is at least an order of magnitude lower than that of the corresponding nickel complexes.

**Fig. 1.** Kinetics of the oxygen absorption by dimethyl sulfoxide at 100 °C and $w_j = 1.5 \times 10^{-7}$ mol L$^{-1}$ s$^{-1}$ without an inhibitor (I) and in the presence of nickel complexes (2--9): 3.33 $\times$ 10$^{-4}$ M Ni(ClO$_4$)$_2$, 6H$_2$O (2); 3.54 $\times$ 10$^{-4}$ M of 2 (3); 3.45 $\times$ 10$^{-4}$ M of 5 (4); 3.39 $\times$ 10$^{-4}$ M of 3 (5); 3.24 $\times$ 10$^{-4}$ M of 4 (6); 2.93 $\times$ 10$^{-4}$ M of 7 (7); 2.66 $\times$ 10$^{-4}$ M of 6 (8); 3.09 $\times$ 10$^{-4}$ M of 1 (9).