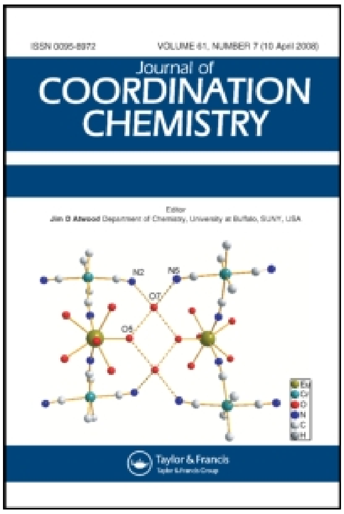

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Further Studies of Nitrodithioacetates of Ni(II), Pd(II) and Pt(II)

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SHORT COMMUNICATION

Further Studies of Nitrodithioacetates of Ni(II), Pd(II) and Pt(II)

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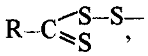
Ni(II), Pd(II), and Pt(II) complexes of $NO_2CHCS_2^{-2}$ have been prepared, and their i.r and u.v spectra described. Spectroscopic evidence is presented to substantiate the existence of the new species $K_2Ni(NO_2CHCS_2)_2S$, a dithio-perthio carboxylate complex.

INTRODUCTION

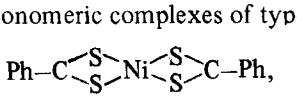
An investigation of the electronic structures and properties of dithio,


$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\diagup S^{-}}{\diagdown S},$$

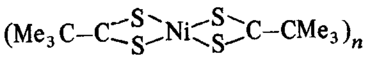
and perthio,


$$\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\diagup S{-}S^{-}}{\diagdown S},$$

carboxylato complexes of Ni(II) has recently been reported.[1,2] Correlation of their spectra with known crystal structures allowed various types to be distinguished: monomeric complexes of type


$$\mathrm{Ph{-}C}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S \diagup}\mathrm{Ni}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S \diagup}\mathrm{C{-}Ph},$$

binuclear complexes, with bridging aliphatic dithiocarboxylate and Ni–Ni bonding of type $(PhCH_2CS_2)_4Ni_2$, which does not survive in solution, monomeric aliphatic complexes without bridging ligands in solution and polymeric, either in the solid state or in concentrated solution, of type


$$(\mathrm{Me_3C{-}C}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S \diagup}\mathrm{Ni}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S \diagup}\mathrm{C{-}CMe_3})_n$$

all of which are based on the planar (NiS_4) chromophore. We are now extending this work to investigate the effect of varying electronic effects of the substituents starting with dithio-carboxylato ligands having negatively charged substituent groups in the α-position with respect to the dithiocarboxylato group, e.g. $C_6F_5CS_2^-$; $CF_3CS_2^-$; $C_6H_5CHCNCS_2^-$ and $NO_2CHCS_2^{2-}$.† This paper reports the Ni(II), Pd(II), and Pt(II) complexes of the last-mentioned ligand.

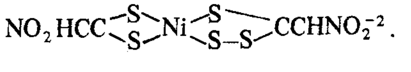
RESULTS

All the complexes obtained are anionic and presumably contain the (MS_4) chromophore. Some have previously been examined by Fackler, *et al.*, who classified them as dithiolate complexes.[4,6]

The same authors noted that $Ni(NED)_2^{2-}$ reacts with iodine or elemental sulphur to give the anionic complex $Ni(S_3CCHNO_2)_2^{2-}$, a bis-perthiocomplex which in turn can revert with triphenylphosphine to the original 1, 1-dithiolato complex in high yield.[4,7]

We repeated the preparations by Fackler, *et al.*, as well as some new preparation of similar compounds, and investigated their physico chemical properties more thoroughly. We thus observed that the i.r. and u.v. spectra in the solid are characteristic of dithiolate complexes, while the chemical properties and electronic spectrum of $Ni(NED)_2^{2-}$ in aqueous solution are more in keeping with those of dithiocarboxylato complexes.

In addition, $Ni(NED)_2^{2-}$ reacts in aqueous solution to give a new anionic complex, in low yield, showing similar u.v. and n.m.r. spectra as those of the dithio-perthiocarboxylato complex:


$$\mathrm{NO_2HCC}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S \diagup}\mathrm{Ni}\genfrac{}{}{0pt}{}{\diagup S \diagdown}{\diagdown S{-}S \diagup}\mathrm{CCHNO_2^{-2}}.$$

---

†abbr. NED: 1,nitroethylene-2,2-dithiolato.

This reacts with triphenylphosphine to give the original $Ni(NED)_2{}^{2-}$, as in reaction (1):

$$Ni(S_3CCHNO_2)_2{}^{2-} + 2PPh_3, \longrightarrow 2SPPh_3 + Ni(NED)_2{}^{2-} \quad (1)$$

On the other hand, both the Pd(II) and Pt(II) complexes do not change between the solid state and solution, and remain stable in solution.

PREPARATION AND PROPERTIES

Dipotassium nitrodithioacetate was prepared as described by Freud.[3]

$Ni(NED)_2{}^{2-}$, $Pd(NED)_2{}^{2-}$ and $Pt(NED)_2{}^{2-}$ have been prepared by Fackler (4), but with benzyltriphenylphosphonium as cation, and not potassium. The potassium salts are obtained by mixing a slight excess of K_2NED with a concentrated aqueous solution of the metal chloride. The complex precipitates immediately (70% yield).

$K_2Ni(NED)_2S$

This is formed by the decomposition of $K_2Ni(NED)_2$ in water. The colour of the solution changes from blue to deep violet on standing for ca. 2 hrs. The mixture is evaporated to dryness and the residue extracted with absolute ethanol. The violet compound is moderately soluble (satured solution $= 5.10^{-3}M$) and the blue compound insoluble in ethanol. Addition of petroleum ether and cooling of the solution gave the compound as a brown-violet solid, containing ethanol of crystallization.

(Found. C 12.53; H 0.86; N 6.37; S 34.87; Ni 12.74; K 16.83; calcd. for $K_2NiC_4H_2N_2O_4S_5.½C_2H_5OH$: C 12.98; H 1.09; N 6.06; S 34.67; K 16.91; Ni 12.69).

The same compound is formed on mixing $NiCl_2 . 6H_2O$ with an aged solution of the ligand, or a fresh solution to which HCl has been added.

The dipotassium salt is stable as a solid, but decomposes in water. The above points indicate that the following reactions are involved:

TABLE I

Infrared absorption bands (cm^{-1}) of K_2NED, $K_2Ni(NED)_2$, $K_2Ni(NED)_2S$, $K_2Pd(NED)_2$, $K_2Pt(NED)_2$ and 1,1-bis(methylthio)2-nitroethylene[a]

K_2NED	$O_2N\text{-}CH{=}C(SCH_3)_2$[b]	$K_2Ni(NED)_2$	$K_2Pd(NED)_2$	$K_2Pt(NED)_2$	$K_2Ni(NED)_2S$	Correlation
1380 s	1510 s	1490 vs	1490 vs	1490 vs	1430 m	$\nu_{as}(NO_2)$
1410 vs	1420 vs	1380 s	1380 s	1380 s	1320 m	$\nu(N\text{-}CH{=}C)$
1220 s	1300 vs	1310 vs	1310 vs	1305 vs		$\nu_{as}(CS_2)$
1177 s	1260 vs	1230 vs	1230 vs	1230 vs	1240 vs	$\nu_s(NO_2)$
1000 s	1035 m	1025 m	1020 m	1020 m	1020 m	$\delta_{ap}(CH)$
					960 m	
920 vs	922 s	915 s	905 s	910 s	940 s	$\nu_s(CS_2)$
					810 w	
735 s	785 s	775 m	760 m	760 m	770 m	$\nu(C\text{-}N)$
698 m	675 s	720 s	715 s	715 s	730 s	$\nu(N\text{-}CH{=}C)$
					700 w	
545 m		520 m	515 m	510 w	520 m	$r(NO_2)$
					480 w	$\nu(S\text{-}S)$
		385 s	330 s	330 m	400 w	$(M\text{-}S)$

[a] Spectra recorded from nujol mulls.
[b] From ref. 5.

$$CHNO_2CS_2^{2-} \underset{OH^-}{\overset{H+}{\rightleftharpoons}} CH_2NO_2^- + CS_2 \qquad (1)$$

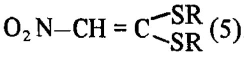
$$\begin{aligned} 3CS_2 + 6OH^- &\longrightarrow CO_3^{-2} + 2CS_3^{-2} + 3H_2O \\ CS_3^{-2} &\longrightarrow CS_2 + S^{-2} \\ S^{-2} + H_2O &\longrightarrow SH^- + OH^- \\ 2SH^- + O &\longrightarrow S_2^{-2} + H_2O \end{aligned} \qquad (2)$$

$$CHNO_2CS_2^{2-} + S_2^{2-} \longrightarrow CHNO_2CS_3^{2-} + S^{2-} \qquad (3)$$

Perthiocarboxylates may be prepared from analogous dithiocarboxylate by oxidation of one of the two sulphur atoms by a polysulphide solution,[7] as shown in 3); reaction 1) leads to re-formation of the ligand, whilst the group of reactions 2) are well-known in the literature.[8]

DISCUSSION

From i.r. spectra and chemical behaviour the dianion of nitrodithioacetic acid may be described as a resonance hybrid of formule I–II. Some reactions are more in agreement with formula I. Thus K_2NED reacts with methyl- or ethyl-bromide to give thioacetals of nitroketene:



$$O_2N{-}CH = C\begin{matrix}\nearrow SR\\ \searrow SR\end{matrix} \quad (5).$$

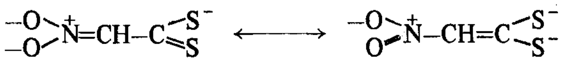
Attempts to prepare derivates of K_2NED from nitroethane have not, however, been successful, xanthates being the products obtained from alcoholic solutions.

The difference in reactivity between nitromethane and nitroethane is surprising. It cannot be due to differences in acidity, but, presumably, is connected with the steric influence of the CH_3 substituent in the α-position to the nitrogroup.

The p.m.r. data unequivocally show that the species $K_2Ni(NED)_2S$ must be formulated as a dithio-perthio compound. The p.m.r. shows two singlets at 2.22 and 2.66τ while that of $K_2Ni(NED)_2$ gives only a single signal at 2.83τ. These results agree with the known n.m.r. behaviour of other dithio and perthio-carboxylates.[7,9]

All the complexes contain the planar (MS_4) chromophore, as suggest by Fackler.[4]

Their reflectance spectra show strong transitions (probably) essentially of c.t. M → L* type at ca. 18.7, 21.1 and 18.8 kK for Ni, Pd and Pt, respectively. The same Ni⟨Pd⟩Pt sequence also occurs in other dithiolate complexes.[11,12] As previously observed by Fackler no low-intensity d–d bands could be observed since they are obscured by high intensity u.v. absorption. The i.r. spectra of all the complexes as solids, are in agreement with a ligand structure corresponding to resonance form II:



I II

since they resemble that of $O_2N{-}CH = C(SCH_3)_2$.

It may be noted that one can expect substantially free rotation of the NO_2 group in II, and this probably also occurs in the solid state for the complexes. However, the i.r. spectrum of K_2NED shows that form I must also be taken into account. It has no absorption bands in the C = C region, whereas aliphatic nitrocompounds normally exhibit strong absorption near 1550 cm^{-1}, and salts of aci-nitrocompounds show a strong band near 1600 cm^{-1}.[15]

The i.r. spectral behaviour of mixed dithioperthio compounds is expected to be complicated by the presence of two different ligands in the same molecule. However, the band at 480 cm_{-1}. may be assigned to the $\tilde{\nu}$ stretch (S–S) vibration.[13] The band of medium strong intensity at 385 cm^{-1} (Ni) and 330 (Pd and Pt) may be assigned to $\tilde{\nu}$ (M–S).

For comparison, the $\tilde{\nu}$ (M–S) frequencies, in $Ni(CS_3)_2{}^{2-}$ fall at 380 cm^{-1} (14), and similar frequencies are found for bis(dithiolate)nickel(II).[10]

As mentioned previously, there is a clear change in visible spectrum when $K_2Ni(NED)_2$ is dissolved in water. The high intensity band at 18.9 kK in the solid is shifted to 16.9 kK (log ϵ = 4.08), the latter spectrum being very similar to that of $Ni(PhCS_2)_2$ a planar molecule with the high intensity band at 16.80 (log ϵ = 3.96).[2] This suggests that the ligand tends more towards resonance form I. This would force the NO_2 group into the same plane as the NiS_4 chromophore, i.e. the whole molecule is planar.

Finally, in the sulphur-rich species $K_2Ni(NED)_2S$ formed by decomposition of $K_2Ni(NED)_2$ in water, the visible region shows a high intensity band at 19.0 kK (log ϵ = 4.29). This spectrum is the same for both solid and solution, and is very similar to that of $Ni(S_2CPh)(S_3CPh)$ (19.0 kK, log ϵ = 3.90).[2]

These data also agree with a dithio-perthio structure for $K_2Ni(NED)_2S$. This new dithio-perthio complexes amazingly like (dithio-perthiobenzoato)-nickel(II) not only so far as concerns electronic spectrum but also in chemical stability and ease of formation. Aliphatic perthio-carboxylates are usually

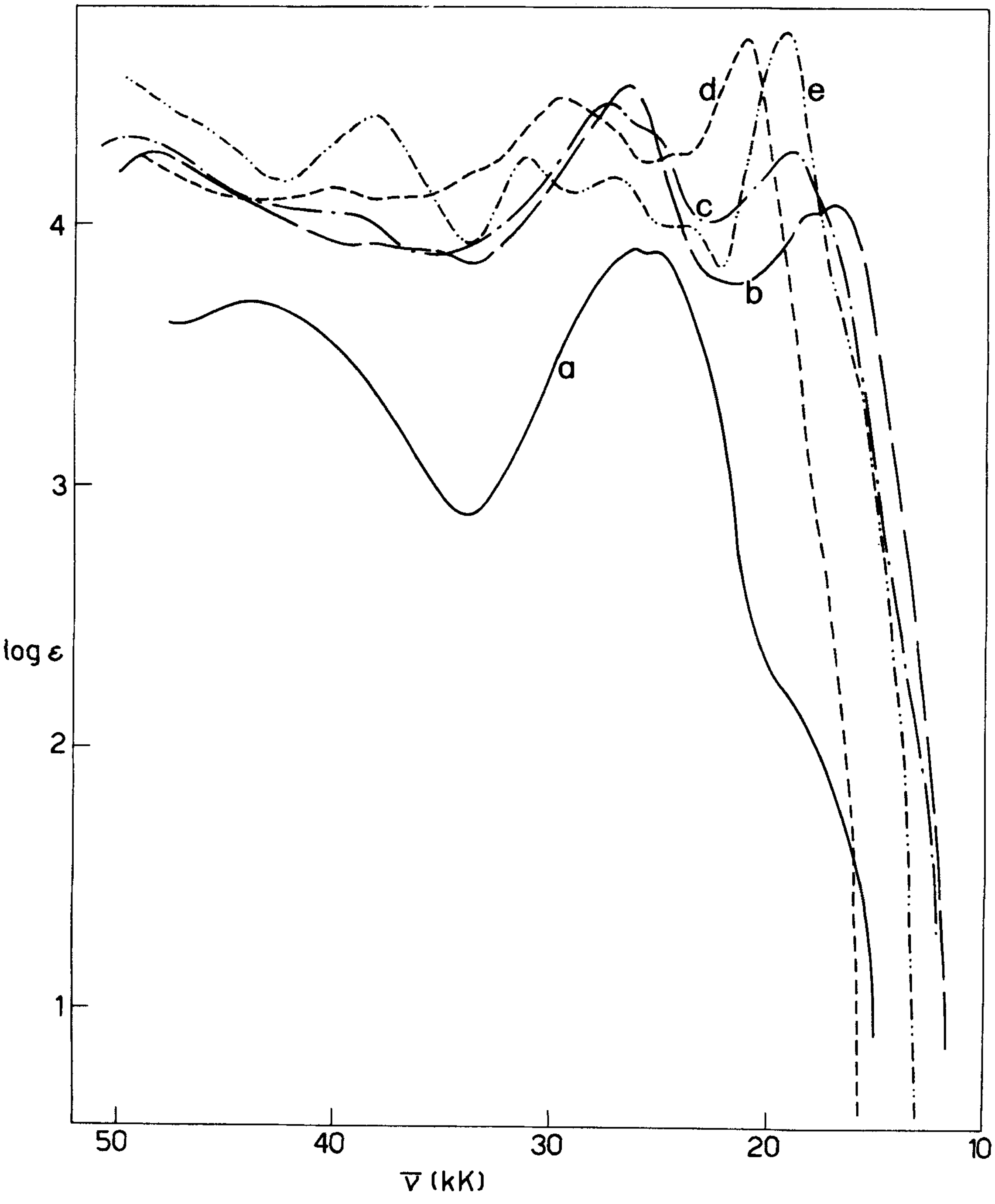


FIGURE 1 Absorption spectra in H_2O: a) K_2NED; b) $K_2Ni(NED)_2$; c) $K_2Ni(NED)_2S$; d) K_2 $Pd(NED)_2$; e) $K_2Pt(NED)_2$.

unstable, the only other exception being the perthiopivalate.[1]

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