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New Nickel(II) Tris-Chelates of O-Alkyldithio-, -Thioseleno- and -Diselenocarbonates

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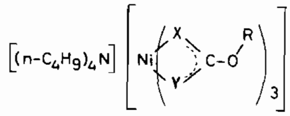
Up to now metal(II) tris-chelates of unsaturated dithioligands are very rare. Only O-alkyldithiocarbonates (xanthates) are known to form tris-complexes with Ni(II) in which all three ligands are bidentate [1–3] whereas Pd(II) and Pt(II) tris-complexes of such ligands are four-coordinated exhibiting a facile intramolecular unidentate–bidentate scrambling process in solution [4].

In this paper we report the synthesis and properties of another two Ni(II) tris-chelates with O-alkylthioseleno- and -diselenocarbonate respectively [1] which are not accessible by the standard method for the sulfur species published elsewhere [3]:



(1)

a) X = S; Y = Se
b) X = Y = Se

R = $(CH_2)_2OCH_3$

Similarly it is possible to prepare a series of mixed ligand complexes [2]:

$$NiL_2 + KL' + (n\text{-}C_4H_9)_4NBr \xrightarrow{\text{acetone}} [(n\text{-}C_4H_9)_4N][NiL_2L'] + KBr\downarrow \qquad (2)$$

$$L, L' \quad (L \neq L') = ROCS_2^-, ROCSSe^-, ROCSe_2^-$$

It turned out that among various alkyls, R = $(CH_2)_2$-OCH_3 yields the thermally most stable complexes [3]. Thus it was used for the experiments in this work.

Experimental

Chemicals

The dithio-, thioseleno-, and diseleno-ligands and the three Ni(II) bis-chelates were isolated and purified in a similar manner as the ethyl compounds described elsewhere [3].

Tetra-n-butylammonium-tris (O-β-methoxyethylthioselenocarbonato)nickelate(II) and the homologous diseleno-ligand chelate were prepared by mixing and stirring the acetonic solutions of the potassium salts of the ligands, nickel chloride hexahydrate (addition of a minimum of methanol), and tetrabutylammonium bromide in equivalent amounts. The potassium bromide precipitate was filtered off. Upon evaporation of some of the solvent at reduced pressure and addition of iso-propanol or ether (in the case of the diseleno-ligand chelate) olive-green crystals deposited which were reprecipitated from acetone–iso-propanol or acetone–ether respectively.

The mixed-ligand chelates $(n\text{-}Bu_4N)[NiL_2L']$ were prepared from an equimolar mixture of a nickel bischelate NiL_2, the potassium salt of a second ligand KL′ and tetrabutylammonium bromide in acetone as described above for the non-mixed chelates.

Physical Measurements

Magnetic susceptibilities were determined at 293 K using a Gouy technique. The calibrant was $[Ni(en)_3]S_2O_3$. Conductivity measurements were made on a model LM 310 conductivity bridge (VEB Hydromat Bannewitz) in nitromethane at 293 K ($c = 10^{-3}$ m). Electronic spectra were recorded on a Beckmann DK-2a and a Specord (VEB Carl Zeiss, Jena) spectrophotometer in acetone solution.

Results and Discussion

All isolated compounds and their properties are summarized in Table I. The color of the crystalline chelates changes from grass-green for a NiS_6 chromophore to green-brown for a $NiSe_6$ arrangement. The preparations and measurements must be done at temperatures not higher than room temperature to prevent possible ligand exchange reactions and because of the fast increase of the thermal instability with increasing selenium content in the coordination sphere. For example, the compound with the $NiSe_6$ chromophore decomposes to a black tacky resin at room temperature within two hours whereas all compounds are stable over weeks at dry-ice temperature. The conductivity values in nitromethane are characteristic for 1:1 electrolytes [5], and the increase of the conductivity with growing Se content in the coordination sphere could be an effect of the decrease of the solution stability. The relative low melting points are probably caused by the different stereoisomers (largest number conceivable for compounds IV, V, and VII).

Because of the similarity of the magnetic moments and the electronic spectra between the sulfur compounds and the selenium-containing complexes prepared in this work, similar molecular structures can be assumed. For the compound $[(n\text{-}C_4H_9)_4N]$

TABLE I. Physical Properties and Analytical Data of Ni(II) Tris-Chelates.

	Compounds[a]	Coordin. Sphere	M.p. (°C)	Λ^c	μ_{eff}^{corr} (B.M.)	Calc %					Found %				
						C	H	N	S	Se	C	H	N	S	Se
I	$(Bu_4N)[Ni(S\text{-}S)_3]^b$	NiS_6	101	50.8	3.21	44.6	7.6	1.9	25.5	–	44.4	7.8	1.8	26.4	–
II	$(Bu_4N)[Ni(S\text{-}S)_2(S\text{-}Se)]$	NiS_5Se	89	52.9	3.08	41.9	7.1	1.7	20.0	9.8	42.3	7.1	1.7	21.7	9.3
III	$(Bu_4N)[Ni(S\text{-}S)_2(Se\text{-}Se)]$	NiS_4Se_2	88	52.7	3.26	39.7	6.7	1.7	15.1	18.6	39.7	6.7	1.8	15.3	18.9
IV	$(Bu_4N)[Ni(S\text{-}Se)_2(S\text{-}S)]$	NiS_4Se_2	85	53.7	3.24	39.7	6.7	1.7	15.1	18.6	40.2	7.1	1.6	16.5	18.6
V	$(Bu_4N)[Ni(S\text{-}Se)_3]$	NiS_3Se_3	79	54.9	3.00	37.5	6.4	1.6	10.8	26.4	38.2	7.0	1.7	11.4	25.9
VI	$(Bu_4N)[Ni(Se\text{-}Se)_2(S\text{-}S)]$	NiS_2Se_4	76	57.5	2.80	35.6	6.1	1.5	6.8	33.5	34.9	6.1	1.5		31.9
VII	$(Bu_4N)[Ni(S\text{-}Se)_2(Se\text{-}Se)]$	NiS_2Se_4	73	61.9	3.04	35.6	6.1	1.5	6.8	33.5	36.1	6.2	1.5	6.5	31.7
VIII	$(Bu_4N)[Ni(Se\text{-}Se)_2(S\text{-}Se)]$	$NiSSe_5$	67	63.5	3.02	33.9	5.8	1.4	3.2	39.9	33.8	5.6	1.3	3.5	38.8
IX	$(Bu_4N)[Ni(Se\text{-}Se)_3]$	$NiSe_6$	71	67.0	3.00	32.4	5.5	1.4	–	44.7	32.4	5.5	1.4	–	45.2

[a] $Bu_4N = (n\text{-}C_4H_9)_4N$; S-S, S-Se, Se-Se = $S_2COC_2H_4OCH_3$, $SSeCOC_2H_4OCH_3$, $Se_2COC_2H_4OCH_3$. [b] Values from [3]. [c] In Ω^{-1} cm^2 mol^{-1}.

TABLE II. Electronic Spectra and Ligand Field Parameters of Three Selected Complexes Compared with the Chromium Complexes (wavenumbers in kK and 1 gε in parentheses).

	Compounds	$^3A_{2g} \to {}^3T_{2g}$ ($=\Delta_0$)	$^3A_{2g} \to a\,^3T_{1g}$	B (K)	β_{35}	f^a	h^a
I	$[Ni(S_2COC_2H_4OCH_3)_3]^-$	9.43 (1.69)	14.8 (1.82)	669	0.64	1.08	3.00
V	$[Ni(SSeCOC_2H_4OCH_3)_3]^-$	9.23 (1.72)	14.4 (1.90)	632	0.61	1.06	3.25
IX	$[Ni(Se_2COC_2H_4OCH_3)_3]^-$	9.08 (1.91)	14.1 (2.09)	606	0.58	1.04	3.50
		$^4A_{2g} \to {}^4T_{2g}$ ($=\Delta_0$)	$^4A_{2g} \to a\,^4T_{1g}$				
X	$Cr(S_2COC_2H_4OCH_3)_3$	15.8 (2.39)	20.3 (2.49)	416	0.45	0.91	2.75
XI	$Cr(SSeCOC_2H_4OCH_3)_3$	15.5 (2.51)	19.5 (2.51)	365	0.40	0.89	3.00
XII	$Cr(Se_2COC_2H_4OCH_3)_3$	15.0 (2.54)	18.6 (2.54)	326	0.36	0.86	3.20

[a] Estimated by the equations Δ = f(ligand) × g(central ion) and $(1 - \beta_{35})$ = h(ligand) × k(central ion) where the functions f and h have been fixed to 1.00 for the hexa-aquo ions, g and k to 8.7 and 0.12 for Ni(II), and to 17.4 and 0.20 for Cr(III) respectively [7].

$[Ni(S_2COC_4H_9^{-n})_3]$ a trigonally distorted NiS_6 octahedron was found [3].

Neglecting the distortion of the octahedron it is possible to estimate the ligand field splitting parameters Δ_0 and the Racah parameters B [6]. In the electronic spectra the first two spin-allowed d–d bands ($^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow a^3T_{1g}$) are observable whereas the third band ($^3A_{2g} \rightarrow b^3T_{1g}$) is hidden under an intense charge-transfer band. Table II shows that the xanthates are weak-field ligands with decreasing strengths on substituting sulfur by selenium (as known for other unsaturated dithio- or diseleno-ligands). However, among all the studied ligands of this type they have the largest Δ_0 values. This is in agreement with publications where Δ_0 was estimated from d^3- or d^6-ion chromophores [8–10] and the parameters for the chromium complexes X, XI, and XII of the ligands used in this work [11]. Although little is known about octahedral Ni(II) complexes with sulfur- or selenium-donor ligands it can be pointed out that saturated ligands, *e.g.* cyclic polyfunctional thioether ligands [12], have larger field strengths than the unsaturated ligands (see also [9]). As expected the nephelauxetic effect increases with growing selenium-content in the coordination sphere.

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