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Nitrato Complexes of Nickel(II) with Aryl(acyl-)thiocarbazides

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The preparation and properties of nitrato complexes of nickel(II) with some substituted aryl(acyl-)thiocarbazides are described. Infrared and electronic spectra in the solid state and the magnetic moments are used to assign the structure of the complexes and to illustrate their properties. The complexes which have the general formulae $[Ni(HL)_2(NO_3)](NO_3)$, *are found to be octahedral with the ligand HL coordinating through the sulphur atom and the end nitrogen atom. The nitrate ions are both ionic and cordinated, the latter acting as bidentate ligands. The electronic parameters of the complexes are also calculated.*

Introduction

In earlier communications we reported several complexes of nickel(II)[1] and cobalt(II)[2] with thiocarbazide derivatives. Three types of complexes of nickel: $[Ni(HL)Cl_2]4H_2O$, $[Ni(HL)_2Cl_2]$ and NiL_2 and four of cobalt: $[Co(HL)_2Cl_2]$, $Co(HL)_2Cl_2$,2 Dioxane $[Co(HL)_2(NO_3)](NO_3)$ and CoL_2 were obtained, the ML_2 complexes of both metals being isomorphous. The thiocarbazide derivatives were found to act as bidentate ligands, utilising both sulphur atom and the end nitrogen atom, except in the complexes of the type $[Ni(HL)_2Cl_2]$, where they are unidentate and sulphur coordinating. In the nitrato complexes of cobalt, the nitrate ions were found both in ionic and cordinated forms, the coordinating species acting as bidentate ligand.

In this paper we report the preparation and the study of the nitrato complexes of nickel(II) with five thiocarbazide derivatives $RCONHNHCSNHNH_2$ (HL) viz. benzoylthiocarbazide (HBTC; R=PhCO), acetylthiocarbazide (ATC; R=MeCO), nicotinoylthiocarbazide (HNTC; R=Nicot-CO), 2-chlorobenzoylthiocarbazide (Cl–HBTC; R=2–ClPhCO), and 2–hydroxybenzoylthiocarbazide (HO–HBTC; R=2–HOPhCO), in order to see whether the ligands as well as the nitrate groups behave in an analogous way to those of the corresponding complexes of cobalt.

Experimental Section

Chemicals. These are all of the reagent grade quality.

Physical Measurements. Electronic spectra in solid state as nujol mull are measured by the Hungarian MOM 201 spectrophotometer No. 87613. Infrared spectra are determined by the KBr disc technique using a Perkin-Elmer Model-221 spectrophotometer. The magnetic susceptibilities are measured with a Gouy balance. X-ray powder diagrams are taken with Nonius Guiner Camera.

Preparation of the $[Ni(HL)_2(NO_3)](NO)_3$ *Complexes.* Nickel(II) nitrate hexahydrate (1 mmole) was dissolved in a minimum volume of ethanol and added to a solution of the ligand (2.5 mmole) dissolved in minimum volume of the same solvent. The resulting solution was concentrated on a water bath to a small volume when the precipitation of the complexes took place. The precipitate was filtered and recrystallised twice from ethanol and in case of insoluble complexes washed thoroughly with hot ethanol.

Results and Discussion

The analytical data for the complexes are given in Table I. The complexes either have very low solubility or are insoluble in all common coordinating solvents. For this reason spectral studies in solution as well as molar conductivity studies could not be carried out. Ionising solvents such as pyridine, dimethylformamide, etc. could not be used, since in these solvents the complexes dissolve with solvation, as indicated by the change in colour (electronic spectra) which accompanies dissolution.

Infrared Spectra. The infrared absorption frequencies of the ligands and of several representative complexes are given in Table II, together with assignments for most of the major peaks. These assignments are based on corresponding assignments in thiosemicarbazide and thiocarbohydrazide[3] and their complexes as well as those discussed by us previoulsly.[1,2] The two band at ~ 1320 cm^{-1} and and ~ 730 cm^{-1} for the ligands are assigned to the νCS modes, both containing contributions from νCN. In the complexes both these bands are much weaker and shifted slightly in lower direction in most cases; this effect has been previously[1,2] ascribed to the involvement of the CS group in coordination.[3,4] Most of the bands assigned

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Table I. Analytical Data

Compound	Colour	Calculated				Found			
		Ni%	N%	S%	Cl%	Ni%	N%	S%	Cl%
$[\mathrm{Ni(HBTC)_2(NO_3)}](\mathrm{NO_3})$	Green	9.73	23.22	10.61	—	9.52	23.62	10.65	—
$[\mathrm{Ni(HATC)_2(NO_3)}](\mathrm{NO_3})$	»	12.26	29.24	13.36	—	12.10	29.36	13.50	—
$[\mathrm{Ni(HNTC)_2(NO_3)}](\mathrm{NO_3})$	»	9.70	27.94	10.58	—	9.55	27.70	10.83	—
$[\mathrm{Ni(Cl\text{-}HBTC)_2(NO_3)}](\mathrm{NO_3})$	»	8.73	20.84	9.52	10.57	8.91	20.54	9.82	10.41
$[\mathrm{Ni(HO\text{-}HBTC)_2(NO_3)}](\mathrm{NO_3})$	Greenish yellow	9.25	21.90	10.08	—	9.51	22.20	10.18	—

Table II. Infrared spectral Data

			Compound			
Assignments	HBTC	$[\mathrm{Ni(HBTC)_2(NO_3)}](\mathrm{NO_3})$	HATC	$[\mathrm{Ni(HATC)_2(NO_3)}](\mathrm{NO_3})$	Cl-HBTC	$[\mathrm{Ni(Cl\text{-}HBTC)_2(NO_3)}](\mathrm{NO_3})$
NH and NH$_2$ stretch	3310(m)					
	3270(m)	3185(wb)	3300(w)			
	3120(M)	3070(wb)	3270(ms)	3220(w)	3305(m)	3280-
		2930(w)	3100(w)	3100(w)	3225(wb)	3030(wb)
Amide I and NH$_2$ bend	1630(ms)	1615(s)	1640(m)	1620(s)	1610(s)	1600(s)
					1590(m)	
Amide II and CM stretch	1530(s)	1535(w)				
		1500(ms)	1570(ms)	1580(w)		
			1510(m)	1520(s)		
					1560(w)	1530(w)
					1550(m)	
CS and CN stretch	1320(s)	1295(w)	1310(s)	1305(w)	1295(ms)	1300(wb)
Amide III	1230(w)	1205(m)	1260(w)			
			1250(w)	1208(ms)		
			1200(w)		1255(w)	
NH$_2$ rock, NCS bend and NH$_2$ deformation	1073(s)	1145(m)				
		1075(ms)				
	1010(s)	1010(ms)	1140(w)	1145(m)	1155(w)	
			1030(w)	1090(s)	1125(w)	
				1000(m)	1100(w)	1080(w)
			1010(w)		1070(ms)	1060(w)
			990(s)		1045(w)	
					1030(w)	
					1010(ms)	
NN stretch		950(m)				
	944(s)	910(w)				
			910(s)	920(m)	940(s)	955(m)
					845(w)	860(w)
NCO, CS and CN stretch	770(m)	770(m)				
	720(s)		760(vw)	760(w)		
	688(s)	680(m)	730(s)	720(w)	755(m)	760(m)
					715(s)	720(w)

s = strong, ms = medium strong, m = medium, w = weak, wb = weak broad, vw = very weak.

to the νNH and νNH$_2$ modes are shifted to lower frequencies in all the complexes, as commonly observed for coordinated $>$NH and –NH$_2$ groups.[5,6]

The infrared spectra of the complexes thus indicate that the two coordination centres of the ligands are the thione sulphur and the hydrazide nitrogen atoms. The possibility of cordination through the oxygen atom or the other nitrogen atoms may be ruled out from the position of the relevant bands listed in Table II.

The bands due to nitrate ions together with their probable assignments are included in Table III. The assignments are made on the basis of Addison and Sutton[7] and the results of other previous studies.[8] In these complexes all the vibrations (ν_1, ν_2, ν_3, and ν_4) of the nitrate group are infrared active; this together with the observed shifts in band positions and the intensities and the splitting of the ν_3 band, clearly shows that some of the nitrate ions are coordinated. On the other hand the presence of the band at ~ 1375 cm^{-1} indicates the existence of ionic nitrate species. Since the ligands act as bidentate and the complexes are octahedral as shown by the electronic spectra and magnetic moments, it is then reasonable to assume that one nitrate ion lies outside the cordination sphere and the other occupies two coordination positions acting as a bidentate ligand.

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Table III. Infrared spectral bands[a] due to the nitrate ions in the nitrate complexes and their assignments

Assignments	$[Ni(HBTC)_2(NO_3)](NO_3)$	$[Ni(HATC)_2(NO_3)](NO_3)$	$[Ni(Cl\text{-}HBTC)_2(NO_3)](NO_3)$
ν_1	1032(m)	1050(ms)	1030(ms)
ν_2	820(m)	830(w)	815(w)
		805(w)	
ν_3	1285(s)	1285(m)	1280(m)
	1345(m)	1340(s)	1350(m)
	1415(s)	1430(s)	1430(w)
		1462(s)	1450(w)
	1380(m)[b]	1380(s)[b]	1375(m)[b]
ν_4	752(ms)	755(ms)	752(s)

[a] sorted out from the i.r. spectra of the complexes. [b] assigned as due to ionic nitrate groups.

Table IV. Electronic spectra and the magnetic susceptibility date at room temperature

Compounds	State	Spectral bands $cm^{-1} \times 10^3$			Dq	β	$\times 10^6$ $\chi_M^{corr.}$	μeff (B.M.)
$[Ni(HBTC)_2(NO_3)](NO_3)$	Nujol	26.60	15.40	[a]	[a]	[a]	47.63.05	3.39
$[Ni(HATC)_2(NO_3)](NO_3)$	»	26.20	15.40	9.43	943	0.84	4735.29	3.37
$[Ni(HNTC)_2(NO_3)](NO_3)$	»	26.60	15.40	9.52	952	0.78	46.92.04	3.35
$[Ni(Cl\text{-}HBTC)_2(NO_3)](NO_3)$	»	26.30	15.40	9.52	952	0.78	4729.69	3.36
$[Ni(HO\text{-}HBTC)_2(NO_3)](NO_3)$	»	26.20	15.60	9.44	944	0.78	4306.54	3.21

[a] Could not be detected.

Table V. X-ray powder diffraction pattern data

$[Co(HATC)_2(NO_3)](NO_3)$		$[Ni(HATC)_2(NO_3)](NO_3)$	
d_{hkl}	I/I_1	d_{hkl}	I/I_1
7.82	1	7.70	3
6.54	6	6.50	6
6.26	8	6.26	8
5.30	v.w.	5.50	v.w.
4.88	w.	4.85	w.
4.40	v.w.	4.41	1
4.01	4	4.00	4
3.68	10	3.66	10
3.61	w.	3.61	v.w.
3.52	2	3.52	1
3.44	w.	3.43	w.
3.11	v.w.	3.10	v.w.
3.07	w.	3.05	w.
2.99	4	2.98	3
2.93	w.	2.92	w.
2.81	v.w.	2.80	w.
2.73	w.	2.72	v.w.
2.67	1	2.66	1
2.63	w.	2.63	w.
2.52	2	2.53	3
2.46	w.	2.45	w.
2.20	v.w.	2.30	w.
2.14	1	2.13	1
		2.03	w.
1.99	w.	1.98	v.w.

Magnetic Measurements. The room temperature magnetic moments of the complexes are given in Table IV. All the complexes are paramagnetic, with moments of 3.21-3.39 B.M. These values are well within the range normally found for Ni^{II} ion in octahedral fields (2.9-3.4 B.M.).[9] Diamagnetic corrections for the ligands are estimated by a procedure outlined by Figgis and Lewis.[10]

Electronic Spectra. The patterns of the spectra of the complexes are similar to those observed in nickel(II) complexes of distorted octahedral structures[3,11,12] (Table IV). The bands at ~9500 cm^{-1} are assigned to the ν_1, $^3A_2(F) \rightarrow {}^3T_2(F)$, at ~15400 cm^{-1} to ν_2, $^3A_2(F) \rightarrow \rightarrow {}^3T_1(F)$, and at ~26200 cm^{-1} to ν_3, $^3A_2(F) \rightarrow {}^3T_1(P)$ transitions. The values of the electronic parameters Dq and β, calculated[13,14] for the octahedral complexes $[Ni(HL)_2(NO_3)](NO_3)$ except those for the $[Ni(HBTC)_2(NO_3)](NO_3)$ are given in Table IV. The 10 Dq values for the complexes are within the expected range for octahedral nickel(II) complexes being lower than those of substituted thiourea complexes[14] and higher than thiobutylrolactum and N-methylthiobutyrolactum complexes.[11]

X-ray Powder Pattern Studies. The X-ray powder diagram of the $[Ni(HATC)_2(NO_3)](NO_3)$ complex is taken and the d_{hkl} values are compared with those of corresponding $[Co(HATC)_2(NO_3)](NO_3)$ complex.

The positions and the relative intensities of d_{hkl} values of the complexes are given in the Table V. The diagrams show that the complexes are isomorphous with each other; similar cases of isomorphism may be expected for complexes with other ligands thus having similar structures with similar disposition of the ligands and of the nitrato groups.

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