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Coordination of Nickel(II) and Cobalt(II) with N,N'-Dimethylurea. An example of Structural Isomerization in Solid State with Nickel(II)

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Octahedral and mixed octahedral–tetrahedral complexes of nickel(II) and cobalt(II) with N,N'-dimethylurea (L) have been prepared: ML_6Y_2 with M = Ni, Y = Br, I, ClO_4 and with M = Co, Y = I, ClO_4; $NiL_4(NCS)_2$; $[ML_6][MX_4]$ with M = Ni, X = Cl, Br and with M = Co, X = Cl, Br, I, NCS. The structures with the ligand coordinated through the oxygen atom are supported by infrared and electronic spectra and magnetic data.

The blue complex $[NiL_6][NiCl_4]$ is isomerized in solid state into a red pentacoordinated high-spin complex NiL_3Cl_2.

Introduction

The complexes of Co(II) and Ni(II) with symmetrical substituted thioureas with R = methyl or ethyl, are well known. Co(II) gives tetrahedral CoL_2X_2 species [1, 2] whereas Ni(II) exhibits octahedral and tetragonal stereochemistries [3, 4]. The ligands are always bonded through the sulfur atom. On the other hand, the compounds obtained with the symmetrical urea derivatives (DMU = N,N'-dimethylurea and DEU = N,N'-diethylurea) have not been studied, except $MDMU_6(ClO_4)_2$ (M = Mn, Ni, Co) [5], $NiDMU_6Br_2$ [6] and $[CoL_6][CoCl_4]$ with L = DMU and DEU [7]. Therefore we have entered upon the coordination of substituted ureas. In previous works, we have shown an octahedral ($MDEU_6X_2$) and a mixed octahedral–tetrahedral ($[MDEU_6][MX_4]$) structure for Co(II), Ni(II) [8] and Mn(II) [9] and an octahedral geometry for Mn(II) with DMU for the 1:3 and 1:6 stoichiometries [10]. Also, we have undertaken the study of the DMU coordination chemistry with Co(II) and Ni(II) to compare the results with those already obtained.

Experimental

The ligand DMU (Merck A.G., Darmstadt) was used without further purification. The preparations, the analytical methods and the physical measurements have been reported previously [8]. The analytical results are given in Table I.

The 1:3 Ni(II) compounds were difficult to prepare: the blue $NiDMU_3Cl_2$ and pale-blue $NiDMU_3Br_2$ products must be handled in dry atmosphere in a glove-box over P_4O_{10}. These two compounds were very sensitive to the atmospheric moisture and fix a water molecule to give a green octahedral product.

TABLE I. Analytical Results for Ni(II) and Co(II) N,N'-Dimethylurea Complexes.

Compound	Color	Melting Point, °C	% Carbon		% Hydrogen		% Nitrogen		% Metal		% Halogen	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$NiDMU_3Cl_2$	Blue	161°	27.44	27.85	6.14	6.31	21.33	21.44	14.9	14.6	18.0	17.6
	Red	148°		27.30		6.13		21.35		14.8		17.8
$NiDMU_3Br_2$	Pale Blue	147°	22.39	22.66	5.01	5.21	17.40	17.25	12.2	12.25	33.1	33.3
$NiDMU_4(NCS)_2$	Green	153°	31.89	31.76	6.12	6.02	26.56	26.38	11.1	11.2	–	–
$NiDMU_6Br_2$	Green	162°	28.94	28.95	6.48	6.49	22.50	22.43	7.9	8.0	21.4	21.4
$NiDMU_6I_2$	Green	[illegible]	25.70	25.68	5.75	5.84	19.98	19.95	7.0	7.1	30.2	30.0
$NiDMU_6(ClO_4)_2$	Green	[illegible]	27.50	27.56	6.15	6.19	21.38	21.45	7.5	7.5	–	–
$CoDMU_3Cl_2$	Blue		27.42	27.57	6.14	6.18	21.32	20.95	14.95	15.05	18.0	17.9
$CoDMU_3Br_2$	Pale Blue	[illegible]	22.38	22.51	5.01	5.00	17.40	17.43	12.2	12.1	33.1	33.3
$CoDMU_3I_2$	Dark Green	[illegible]	18.73	18.82	4.19	4.27	14.56	14.58	10.2	10.2	44.0	43.6
$CoDMU_3(NCS)_2$	Dark Blue	132°	30.07	30.08	5.51	5.62	25.50	25.34	13.4	13.4	–	–
$CoDMU_6I_2$	Pink	132° dec.	25.70	25.81	5.75	5.85	19.98	19.96	7.0	7.1	30.2	29.9
$CoDMU_6(ClO_4)_2$	Pink	197°	27.49	27.58	6.15	6.31	21.37	21.42	7.5	7.5	–	–

TABLE II. Electronic Reflectance Spectra of Ni(II) Compounds (Band Maxima in kK) and Ligand-field Parameters According to Ref. 8 in cm^{-1}.

Compound Octahedral $^3A_{2g}(F) \rightarrow$ Tetrahedral $^3T_1(F) \rightarrow$	ν_3 oct. $\rightarrow {}^3T_{1g}(P)$	ν_2 oct. $\rightarrow {}^3T_{1g}(F)$ $+ {}^1E_g(D)$	ν_1 oct. $\rightarrow {}^3T_{2g}(F)$	ν_3 tetr. $\rightarrow {}^3T_1(P)$	ν_2 tetr. $\rightarrow {}^3A_2(F)$	Ligand-field Parameters			
						Δ_0	Δ_t	B	β[a]
$[NiDMU_6][NiCl_4]$	24.4	[c]	[d]	14.95	7.65	–	4180	810[e]	0.78
$[NiDMU_6][NiBr_4]$	[b]	[c]	[d]	13.95	7.2	–	3900	750[e]	0.73
$NiDMU_4(NCS)_2$	25.0	14.8 13.4	9.35	–	–	9350	–	800	0.78
$NiDMU_6Br_2$	24.4	15.1sh 13.2	8.5	–	–	8500	–	860	0.83
$NiDMU_6I_2$	24.4	15.3sh 13.2	8.5	–	–	8500	–	860	0.83
$NiDMU_6(ClO_4)_2$	24.4	15.1sh 13.1	8.5	–	–	8500	–	860	0.83

[a] B_0 value for the free Ni^{2+} ion: 1030 cm^{-1}. [b] Masked by charge transfer band of $[NiBr_4]^{2-}$. [c] Masked by ν_3 band of $[NiX_4]^{2-}$. [d] Masked by ν_2 band of $[NiX_4]^{2-}$. [e] B value for $[NiX_4]^{2-}$.

TABLE III. Electronic Reflectance Spectra of Co(II) Compounds (Band Maxima in kK) and Ligand-field Parameters According to Ref. 8 in cm^{-1}.

Compound Octahedral $^4T_{1g}(F) \rightarrow$ Tetrahedral $^4A_2(F) \rightarrow$	Tetr. $\rightarrow$ Doublet States	ν_3 tetr. $\rightarrow {}^4T_1(P)$	ν_2 tetr. $\rightarrow {}^4T_1(F)$ broad	ν_3 oct. $\rightarrow {}^4T_{1g}(P)$	ν_1 oct $\rightarrow {}^4T_{2g}(F)$	Ligand-field Parameters			
						Δ_0	Δ_t	B	β[a]
$[CoDMU_6][CoCl_4]$	26.1sh 24.3 21.9 19.1	15.35	6.5	[b]	[c]	–	3800	700[d]	0.72
$[CoDMU_6][CoBr_4]$	24.9 {23.3 22.8} {21.3 21.1 20.6} 18.3	14.55	5.9	[b]	[c]	–	3200	700[d]	0.72
$[CoDMU_6][CoI_4]$	21.7 {21.1 20.0 19.2} 18.3	13.3	5.3	[b]	8.0	–	2350	690[d]	0.71
$[CoDMU_6][Co(NCS)_4]$	22.9sh 20.9 19.8	16.45	9.3	[b]	[c]	–	4600	700[d]	0.72
$CoDMU_6I_2$	–	–	–	{19.0 20.8sh}	8.15	9250	–	800	0.82
$CoDMU_6(ClO_4)_2$	–	–	–	{19.1 20.8sh}	8.15	9250	–	800	0.82

[a] B_0 value for free Co^{2+} ion: 971 cm^{-1}. [b] Masked by ν_3 band of $[CoX_4]^{2-}$. [c] Masked by ν_2 band of $[CoX_4]^{2-}$.
[d] B value for $[CoX_4]^{2-}$.

TABLE IV. Significant Bands in the Infrared Spectra.

Compound	ν_{N-H} Stretching	$\nu_{C=O}$ Stretching	δ_{N-H} Bending	ν_{C-N} Amide III Band	$\nu_{C'-N}$ Stretching
$DMU(CHCl_3)$	3465vs, 3390sh	1670vs	1560vs	1320s 1270sh	1140m
$NiDMU_3Cl_2$ (blue)	3340vs	1630vs	1575vs	1355s	1175–1150m
$NiDMU_3Br_2$	3390–3270vs	1625vs	1575vs	1355s	1180–1150m
$NiDMU_4(NCS)_2$	3400sh, 3360vs, 3300sh	1630vs	1570vs	1350s	1180–1150m
$NiDMU_6Br_2$	3400–3270vs	1630vs	1570vs	1355s	1185–1150m
$NiDMU_6I_2$	3340–3300vs	1630vs	1570vs	1355s	1175–1150m
$NiDMU_6(ClO_4)_2$	3420sh, 3350vs	1630vs	1575vs	1355s	ν_3 ClO_4^-
$CoDMU_3Cl_2$	3380vs	1630vs	1575vs	1355s	1175–1155m
$CoDMU_3Br_2$	3330vs	1625vs	1570vs	1355s	1188–1150m
$CoDMU_3I_2$	3350vs	1630vs	1575vs	1350s	1180–1150m
$CoDMU_3(NCS)_2$	3350vs	1630vs	1575vs	1355s	1180–1150m
$CoDMU_6I_2$	3340–3300vs	1630vs	1570vs	1355s	1175–1150m
$CoDMU_6(ClO_4)_2$	3420sh, 3350vs	1630vs	1575vs	1355s	ν_3 ClO_4^-

TABLE V. Magnetic Data

Compound	Diamagnetic Correction ($\times 10^6$)	T.I.P. Correction ($\times 10^6$)	$\chi_M^{Corr.}$ ($\times 10^6$)
$[NiDMU_6][NiCl_4]$	–432	245	10450
$[NiDMU_6][NiBr_4]$	–476	245	10200
$NiDMU_4(NCS)_2$	–287	220	4350
$NiDMU_6Br_2$	–407	245	4350
$NiDMU_6I_2$	–439	245	4500
$NiDMU_6(ClO_4)_2$	–402	245	4400
$[CoDMU_6][CoCl_4]$	–432	550	20150
$[CoDMU_6][CoBr_4]$	–476	650	19900
$[CoDMU_6][CoI_4]$	–540	890	20200
$[CoDMU_6][Co(NCS)_4]$	–462	450	16900
$CoDMU_6I_2$	–439	–	10600
$CoDMU_6(ClO_4)_2$	–402	–	10500

Calculated B.M. values for $[NiCl_4]^{2-}$ and $[NiBr_4]^{2-}$ are 3.78 and 3.70 B.M.

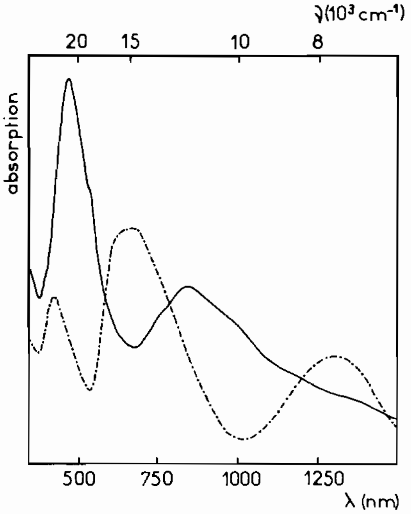

Figure. Reflectance spectra of red $Ni(DMU)_3Cl_2$ (———) and blue $Ni(DMU)_3Cl_2$ (· — · —).

Moreover, the blue $NiDMU_3Cl_2$ complex was transformed at room temperature into a red compound of the same formula after two months. This transformation, in the solid state, could also be obtained by heating at 110 °C for eight hours.

Results and Discussion

General Case

Except for the red $NiDMU_3Cl_2$ complex, the spectral and magnetic data (Tables II to V) are quite similar to those obtained with DEU compounds [8] and lead practically to the same conclusions, *i.e.* a mixed octahedral–tetrahedral structure $[MDMU_6][MX_4]$ for 1:3 stoichiometry and an octahedral one for the other compounds. The ligand DMU is bonded through the oxygen atom and the NCS^- anion through the nitrogen atom in a *trans*-geometry for $NiDMU_4(NCS)_2$ and in the tetrahedral $[Co(NCS)_4]^{2-}$ anion. Electronic spectra, infrared spectra and magnetic data appear to be the sum of those of the two species in the 1:3 complexes except for the Co(II) compounds magnetic data. In these last ones the anions (iodide, perchlorate or tetrahalocobaltate) or/and crystal packing effect cause distortions in the octahedral cation, which change the magnetic susceptibility contribution of the $[CoDMU_6]^{2+}$ species [11]. Besides, powder diffraction patterns show an isomorphism between corresponding Co(II) and Ni(II) compounds.

Structural Study of Red $NiDMU_3Cl_2$ Compound

The red color and particular X-ray powder diagram (different from those of mixed octahedral–tetrahedral $NiDMU_3Cl_2$ and octahedral $MnDMU_3Cl_2$) indicate another geometry for this complex. Magnetic data (5100 × 10^{-6} cgs or 3.46 B.M.) denote a high-spin complex and exclude a tetrahedral–square transformation. The reflectance spectra given in the figure show the difference between the two $NiDMU_3Cl_2$ compounds. The comparison with high-spin pentacoordinated Ni(II) compounds (Table VI) indicates clearly a five-coordinate structure for the red complex.

The X-ray structure determinations of the above compounds (or isomorphous ones) have shown an irregular trigonal bipyramidal structure for $Ni(Me_5$-

TABLE VI. Reflectance Spectra of Five-Coordinate Nickel(II) Compounds

Compound	Observed Band (in kK)[b]							Ref.
$Ni(Me_5dien)Cl_2$[a]	$\underline{21.7}$	18.9		15.7	$\underline{12.7}$	9.6	$\underline{\sim 5.0}$	(12)
$Ni(Me_5dien)Br_2$	$\underline{21.6}$	18.2		15.4	$\underline{12.5}$	11.1; 9.8	$\underline{\sim 5.0}$	(12)
$[Ni(Me_3AsO)_5](ClO_4)_2$	$\underline{22.2}$	19.2	17.2	13.6	$\underline{11.3}$	8.6	$\underline{< 5.0}$	(13)
$[Ni(Me_3AsO)_4ClO_4]ClO_4$	$\underline{22.3}$	19.4	17.2	13.5	$\underline{11.2}$	8.6	$\underline{< 5.0}$	(13)
$NiDMU_3Cl_2$ (red)	$\underline{21.2}$	17.9		13.2	$\underline{11.6}$	9.8	$\underline{4.5}$	

[a] Me_5dien: $CH_3N(CH_2CH_2N(CH_3)_2)_2$.

[b] Underlined values correspond to strong absorptions, the others to shoulders.

dien)X_2 complexes [14] and a square pyramidal for the follower [15]. The electronic spectra are similar for the two configurations, and, therefore, cannot allow the determination of the exact geometrical configuration for the red compound.

The IR spectrum (4000–400 cm^{-1}) is very similar to those given in Table IV. The ligand vibrations are influenced by the donor atoms and only slightly by the geometrical structure. The band shifts ($\nu_{C=O}$ decreases, δ_{N-H}, ν_{C-N}, $\nu_{C'-N}$ increase) indicates a coordination through the oxygen atom and excludes a nitrogen bonding that involves the coordination of the two chlorides. The far IR spectrum exhibits three strong and broad bands (278, 216 and 164 cm^{-1}) which must be assigned to Ni–O and Ni–Cl vibrations without more precise attributions.

Conclusion

This study has shown that the coordination of Co(II) and Ni(II) with urea derivatives (except the red $NiDMU_3Cl_2$ compound) is not modified by the substitution of ethyl groups by methyl in the ligand: the conclusions drawn from the previous paper [8] hold true (mixed octahedral–tetrahedral structure for the 1:3 complexes and octahedral for the others). The 1:3 stoichiometry is also obtained with Mn(II) halides: in the case of DEU the structure is similar to the Ni(II) and Co(II) compounds whereas for DMU a different structure is obtained (octahedral) [10, 16]. This and the instability of the 1:3 nickel complexes are in agreement with the crystal field stabilization energies of the three metallic ions in a tetrahedral field. So the stabilization of the tetrahalometallate anions is greater with the $[MDEU_6]^{2+}$ than with the $[MDMU_6]^{2+}$ cation. On the other hand, the substitution of the oxygen donor atom for the sulfur one in thiourea derivatives involves a wholly different configuration of the obtained coordination compounds: tetragonal NiL_4X_2 [3, 4] and tetrahedral CoL_2X_2 [1, 2].

Moreover, we have also shown the transformation of the blue $[NiDMU_6][NiCl_4]$ ionic solid into a high spin pentacoordinated complex with monodentate ligands:

$$\underset{\text{blue}}{[NiDMU_6]\,[NiCl_4]} \xrightarrow[\text{8 hours}]{110^{\circ}C} \underset{\text{red}}{2NiDMU_3Cl_2}$$

This reaction which necessitates a migration of the ligands takes also place very slowly at room temperature but it does not occur with the other mixed octahedral–tetrahedral Ni(II) compounds. This isomerization brings out the structural lability of Ni(II). Five-coordinate configuration is generally less stable than the other ones. Most of these complexes are obtained with polydentate ligands which give an additional stability due to structural rigidity, therefore pentacoordinated Ni(II) complexes with monodentate ligands are rare. The five-coordinate compound is high-spin as is generally observed with the strongly electronegative elements N and/or O as ligand atoms. Unfortunately in the absence of a direct X-ray structure determination, the exact stereochemical arrangement of the five coordinating atoms is not possible.

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